



A STUDY ON
THE SOURCE OF ANOMALOUS ARSENIC CONCENTRATIONS IN SOILS FROM
THE GLOBEVILLE COMMUNITY— DENVER, COLORADO.

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ABBREVIATIONS

CDPHE	Colorado Department of Health and Environment
EMPA	Electron Microprobe Analysis
EDSXRF	Energy Dispersive Spectrometer X-ray Fluorescence
SOP	Standard Operating Procedure
CAGO	Colorado Attorney Generals Office

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1.0 INTRODUCTION

On April 15, 1997 EnviroGroup Limited, on behalf of ASARCO, submitted a report entitled: "Evaluation of Anomalous Arsenic Concentrations in Surface Soils" to the CDPHE. The ASARCO report attempted to demonstrate that certain anomalous levels of arsenic at the Globe site were not caused by the ASARCO Globe Plant but, rather, were the result of residential use of PAX (a commercial pesticide). In response to that study, CDPHE requested that I review the ASARCO report to assist CDPHE in determining the adequacy of ASARCO's demonstration. As part of this evaluation, I conducted a mineralogical and geochemical study on community and plant (Globe-ASARCO Plant) soils primarily to characterize the form(s) of arsenic and occurrence of related metals (Pb, Se, Tl, Sb, In, and Cd) found in the soils. The purpose of this study was to evaluate data presented in the ASARCO report; specifically the source of the anomalously high (300-3800 mg/kg) arsenic concentrations found in apparently isolated portions of the site. Samples were acquired from three sources: the ASARCO study, CDPHE, and a community representative. A site map, with sample locations and selected demographics, are indicated on Figure 1.

2.0 HISTORICAL BACKGROUND

[Portions of this section have been excerpted because the information is based on documents subject to Protective Order, and ASARCO has to date not given consent for their release.]

The Globe Smelter, originally called the Holden Smelter, was constructed in 1886. It was originally built to process the rich lead and copper ores of Colorado and Idaho. The facility consisted of fifteen reverberatory furnaces, two Brown-O'Hara furnaces and twelve Bruchner furnaces for roasting operations, while smelting was carried out in the seven blast furnaces constructed at the facility. The facility, along with the Omaha Grant Smelter, were acquired by the American Smelting and Refining Company in 1898. Baghouses (devices that minimize stack emissions) were introduced to the facility in the early 1900's to limit the loss of metal from fumes.

During the period from 1905 to 1910, a mill, ten hand roasters, and eight Godfrey roasters were added to the facility. From 1910 to 1915 many of the older roasters were replaced with mechanical systems. In 1911 the Globe facility began roasting arsenic, which was recovered from baghouse dusts shipped by railroad from numerous smelters (Leadville, Chihuahua, San Luis, Murray, Helena, El Paso, Selby, and Federal) around the country. From 1911 to 1927, arsenic production (both black and white arsenic) was the primary source of income for the facility, as lead smelting was abandoned and much of the associated equipment was dismantled

and moved to other plants. During this period (1926) ASARCO applied to the state of California to register "Tacoma Brand" rat killer, their arsenic trioxide rodenticide. Arsenic (As_2O_3) production remained an important commodity until 1927, when these facilities were closed.

Although arsenic was no longer the commercially dominant product after 1927, the Globe plant was processing baghouse dusts with high arsenic concentrations and sold arsenic products. Since 1927 the facility's operations primarily have been associated with the production of cadmium, lead, and thallium, with minor production of indium, selenium, antimony, zinc, gold, silver, tellurium, and bismuth. Processing of these materials from baghouse dusts still produced significant arsenic concentrations in the smoke emitted from the facility. As late as 1973, approximately 17,000 lbs. of commercial arsenic (As_2O_3) were sold from the Globe facilities (CAGO-98#19839), and in 1974, 20,000 lbs. of arsenic trioxide was scheduled to be shipped to the Omaha plant (CAGO-98 Box 4, File #60).

Since the 1980s until approximately 1993, cadmium, thallium, indium, selenium and lead have been the primary commercial products refined at the facility. A significant amount of demolition and contaminant clean-up have also been undertaken.

3.0 ARSENIC GEOCHEMISTRY

Arsenic is found in many minerals and is typically enriched in soils originating from shales/schists and argillaceous sediments. Uncontaminated soils have mean concentrations of 5-10 mg/kg (Fergusson, 1990), worldwide. The lowest levels typically are found in sandy soils derived from granites, as are those in the Globeville area, and average 4 mg/kg. The arid to semi-arid climate in the Denver area along with the near neutral (6-8.5 pH) acidity of the local soils stimulate very low metal mobility, generally concentrating metals in the surface horizons by preventing their downward distribution over time. Mobility may be enhanced by irrigation, aeration, or by utilization of soil amendments. In particular, phosphate fertilizers can significantly increase the mobility of arsenic (Logan and Chaney, 1983).

Numerous sources of arsenic have led to elevated concentrations in surface soils. Table 1 is a compilation of the most common sources, their arsenic speciation, along with associated arsenic-soil concentrations (data from Barzi et al., 1996, Kabata and Pendias, 1993; Fergusson, 1990; and Drexler, per. communication, 1998).

Table 1. Compilation of common arsenic sources and associated soil-arsenic concentrations.

Source	Arsenic Speciation	Associated Soils As mg/kg
Mining	Sulfosalts, As_2S_3 , $FeAsS$	23-1023
Chemical Works	$PbAsO$, As_2O_3 , $R^{**}AsO$	10-2000
Metal Processing	As_2O_3 , AsM^*O , $PbAsO$	33-2500
Application of Pesticides	As_2O_3 , $PbAsO$, $R^{**}AsO$, Na-Ca arsenates	38-625
Gardens and orchards	$PbAsO$	38-892
Fly Ash	Unknown	1-9
Municipal Sludge	Unknown	1-6
Sheep/Cattle Dip/Tannery	As_2O_3	300-1000
Wood Preservatives	Cr-Cu arsenates	10-2000

**R = Organic compounds, *M = typically Pb, Ca, Cd, or Sb.

4.0 ARSENIC SPECIATION

Ten samples from the Globe/ASARCO facility (Table 2) and thirty samples from the surrounding community (Table 3) were speciated for arsenic using electron microprobe (EMPA) techniques. Methodologies used for sample preparation, data collection, and data synthesis are described below. Although this report emphasizes the species of arsenic found in the various media, data also were collected on lead, indium, thallium, cadmium, and selenium.

Table 2.0 Globe/ASARCO plant sample set.

Sample ID.	Sample No.	Source	As mg/kg	Pb mg/kg	Cd mg/kg	Zn mg/kg
609611	AN28A	Sediment Pond	16300	760	4570	1590
609613	AO25A	Sediment Pond	10200	1600	2530	1030
609608	53R18179	Stack Fallout	402	496	271	922
609602	51R1900	Stack Fallout	195	457	45	531
609603	55M0500	Stack Fallout	282	592	51	297
609601	53D06003	Stack Fallout	189	500	246	1726
609626	AL24B	Roaster Stack	15400	2740	6680	1900
609625	AK24B	Roaster Stack	13300	5800	7200	3250
609616	AQ11A	Roaster Stack	14700	53000	12400	21800
609623	M02A	Plant Background Soil	14	170	23	215

Table 3.0 Globeville community soil samples used for arsenic speciation.

Sample ID.	Property No.	Address	As mg/kg	Pb mg/kg	Cd mg/kg	Zn mg/kg
610604	49E10	4992 Lincoln	3873	889	31	697
610606	49N10	4977 Pearl	800	1310	66	1371
609608	53R18179	Vacant Lot, Washington	402	496	271	NA
609618	45E31	4500 Lincoln	<10	137	<10	234
609619	45L16	4519 Pennsylvania	862	654	5	447
609630	45F23	4535 Sherman	524	1022	<10	568
609629	45F24	4541 Sherman	720	1617	<10	712
609631	45G08	4548 Sherman	516	738	<10	296
609628	45J180	4523 Logan	1524	736	11	540
609620	45J200	4529 Logan	1348	946	20	665
609627	45L160	4519 Pennsylvania	20	192	<10	253
609617	45M100	4600 Grant	13	192	<10	250
		4363 Lincoln-R	81	251	6	NA
		4438 Lincoln-F	2200	741	17	NA
		4422 Delaware-F	136	529	7	NA
		4428 Lincoln-F	459	376	13	NA
GV-4		4460 Pennsylvania	779	533	12	NA
GV-4		4460 Pennsylvania-R	441	439	12	NA
GV-4		4460 Pennsylvania-F	200	744	13	NA
GV-5		4524 Pearl	47*	145*	4*	NA
		4425 Pennsylvania-F	43	210	6	NA
SO-1		4815 St. Paul	107	130	3	NA
SO-7		4659 Williams	93	437	7	NA
SO-10		4715 Williams	118	235	8	NA
SO-13		4684 Race	63	304	8	NA
SO-14		4709 Race	75	327	6	NA
SO-15		4718 Race	1800	754	13	NA
SO-16		4722 Race	30	431	9	NA
SO-22		4639 Vinc	55	310	5	NA
9190		55013 003A	116	296	26	163
770		55015 008E	181	459	33	369
9232		55013 004B	103	923	12	468
9742		55019 003A	168	265	21	169
9779		55019 003B	146	185	13	137
0071		55N02 002B	170	180	47	230

NA = Not analyzed for. * average of duplicate analysis.

4.1 Methodology

Metal speciation was conducted on a JEOL 8600 electron microprobe (EMPA), operating at 15Kv (accelerating voltage) and 15-20 nanoAmps current, at the Laboratory for Geological Studies at the University of Colorado following the laboratory's SOP (Appendix I). One exception was made in the SOP, in that the samples were not sieved to $<250\ \mu\text{m}$, as is most common for bioavailability determinations, but the 2mm fraction was used in order to be consistent with previous site studies. Sample preparation is described in Appendices I and II. The samples were all air dried and prepared for speciation analysis as outlined in the SOP. A combination of both an Energy Dispersive Spectrometer (EDS) and a Wavelength Dispersive Spectrometer (WDS) were used to collect x-ray spectra and determine elemental concentrations on observed mineral phases. All quantitative analyses are based on certified mineral and metal standards using a Phi Rho Z correction procedure. Representative backscatter photomicrographs (BSPM) illustrating sample characteristics were acquired.

Data from EMPA is set forth in Table 4 and will be summarized using three methods. QA/QC data are included in Appendix II. The first method is the determination of FREQUENCY OF OCCURRENCE (F). This is calculated by summing the longest dimension of all the arsenic-bearing phases observed and then dividing each phase by the total length for all phases.

Table 4. Summary of Speciation Results from the Globeville Area.

Sample	53D08003			4363 Lincoln-R			4992 Lincoln		
Location*	609601			R			610604		
As (ppm)	P			81			3873		
	Freq%	RM%	Min-ppm	Freq%	RM%	Min-ppm	Freq%	RM%	
Slag	92.4%	58.0%	109.6						
Clays	1.8%	3.5%	6.5						
Fe Oxide	5.8%	38.6%	72.9	50.0%	86.0%	69.6	18.3%	0.9%	33.5
PbSiO ₄				40.0%					
Phosphate				10.0%	14.0%	11.3	1.4%	0.1%	2.1
As ₂ O ₃							62.3%	88.8%	3437.5
AsSbO							5.0%	5.7%	219.3
Mn Oxide							5.4%	0.2%	5.9
PbAsO							7.6%	4.5%	174.8
AsCdO									
Cerussite									
Galena									
PbMO									
PbO									
Solder									
Fe Sulfate									
AsMO									
CaAsO									
Pb									
Gypsum									
Anglesite									
PbCl ₄									
AlAsO									
Aspy									
AsFeO									
Paint									
SS									
CdO									
PbVan									
In (Indicated if observed)									
Se (Indicated if observed)									
Total Particles Counted	6			4			100		

*Location: P= Plant, R= Residential and C= Commercial

Table 4. Summary of Speciation Results from the Globeville Area.

Sample	51R1900 609602			55M0500 609603			AN28A 609611			AO25A 609613		
Location*	P			P			P			P		
As (ppm)	195			282			16300			10200		
	Freq%	RM%	Min-ppm	Freq%	RM%	Min-ppm	Freq%	RM%	Min-ppm	Freq%	RM%	Min-ppm
Slag	24.6%	2.3%	4.4									
Clays				4.0%	0.9%	2.7	1.0%	0.0%	3.2	4.4%	0.1%	12.2
Fe Oxide	21.1%	20.7%	40.3	47.9%	40.1%	113.1	4.4%	0.3%	49.4	12.0%	1.2%	117.8
PbSiO ₄												
Phosphate	16.1%	12.8%	25.1	31.8%	21.7%	61.2						
As ₂ O ₃							15.1%	31.2%	5079.4			
AsSbO												
Mn Oxide	30.8%	18.1%	35.3	13.4%	6.7%	18.9						
PbAsO	2.3%	28.1%	54.9	1.5%	15.8%	44.7	7.5%	6.4%	1047.3	6.1%	7.4%	758.3
AsCdO	0.9%	11.9%	23.3	1.3%	14.7%	41.5						
Cerussite	0.8%											
Galena	0.5%											
PbMO	0.9%	5.1%	10.0				1.2%	0.5%	76.9			
PbO	0.6%	0.4%	0.8									
Solder	0.9%	0.0%										
Fe Sulfate	0.6%	0.5%	0.9									
AsMO							51.4%	45.9%	7484.6	27.6%	34.8%	3552.9
CaAsO							19.0%	15.7%	2559.1	48.3%	56.4%	5756.9
Pb										0.0%	0.0%	0.0
Gypsum										1.5%	0.0%	1.9
Anglesite												
PbCl ₄												
AlAsO												
Aspy												
AsFeO												
Paint												
SS												
CdO												
PbVan												
In (Indicated If observed)	In						In			In		
Se (Indicated If observed)							Se			Se		
Total Particles Counted	93			34			156			93		

*Location: P= Plant, R= Residential and C= Commercial

Table 4. Summary of Speciation Results from the Globeville Area.

Sample	AQ11A 609616			4600 Grant 609617			45L16 609619			AK24B 609625		
Location*	P			R			R			P		
As (ppm)	14700			13			862			13300		
	Freq%	RM%	Min-ppm	Freq%	RM%	Min-ppm	Freq%	RM%	Min-ppm	Freq%	RM%	Min-ppm
Slag												
Clays												
Fe Oxide	0.5%	0.1%	15.9				37.9%	4.0%	34.1	10.8%	1.0%	128.8
PbSiO ₄	0.3%											
Phosphate				20.0%	1.8%	0.2	17.8%	1.5%	13.0			
As ₂ O ₃							25.1%	79.1%	682.0			
AsSbO												
Mn Oxide							7.8%	0.5%	4.2			
PbAsO	1.6%	4.2%	612.1				10.4%	13.7%	117.8	19.1%	21.6%	2868.5
AsCdO												
Cerussite	11.1%											
Galena												
PbMO	75.5%	88.1%	12952.7	20.0%	12.3%	1.6	0.1%	0.1%	0.6			
PbO	1.3%	0.2%	31.2									
Solder												
Fe Sulfate	3.8%	0.7%	97.3							4.7%	0.4%	47.9
AsMO	2.5%	6.7%	990.7	60.0%	85.9%	11.2	0.9%	1.2%	10.3	64.8%	76.6%	10183.2
CaAsO										0.5%	0.5%	71.7
Pb												
Gypsum												
Anglesite	2.4%									0.1%		
PbCl ₄	1.0%											
AlAsO												
Aspy												
AsFeO												
Paint												
SS												
CdO												
PbVan												
In (Indicated If observed)	In											
Se (Indicated If observed)										Se		
Total Particles Counted	114			3			102			283		

*Location: P= Plant, R= Residential and C= Commercial

Table 4. Summary of Speciation Results from the Globeville Area.

Sample	AL24B			45L160			45J180Dup			45F24Dup		
Location*	609626			609627			609628			609629		
As (ppm)	P			R			R			R		
	15400			20			1524			720		
Slag	Freq%	RM%	Min-ppm	Freq%	RM%	Min-ppm	Freq%	RM%	Min-ppm	Freq%	RM%	Min-ppm
Clays												
Fe Oxide	5.9%	0.5%	77.4	11.4%	16.8%	3.3	15.5%	2.7%	41.1	0.5%	0.0%	0.1
PbSiO4										18.2%	1.9%	13.4
Phosphate				68.8%	83.0%	16.6	7.9%	1.1%	16.6	1.3%		
As2O3							15.1%	80.9%	1232.9	27.0%	2.2%	16.1
AsSbO										22.7%	70.0%	503.7
Mn Oxide							8.2%	0.9%	13.7	1.0%	2.5%	17.7
PbAsO	9.7%	10.5%	1615.0				2.2%	5.0%	76.2	7.8%	0.5%	3.4
AsCdO										17.2%	22.0%	158.2
Cerussite												
Galena												
PbMO	6.0%	2.9%	447.9									
PbO												
Solder												
Fe Sulfate				8.5%	0.2%	0.1						
AsMO	59.5%	66.9%	10307.9							1.8%	0.0%	
CaAsO										0.4%	0.0%	
Pb							4.0%	9.4%	143.2	0.7%	1.0%	0.3
Gypsum												7.1
Anglesite	1.6%											
PbCl4				11.4%								
AlAsO	2.2%	0.0%	2.7							0.4%		
Aspy	0.5%	1.4%	216.8									
AsFeO	14.6%	17.7%	2732.3									
Paint												
SS												
CdO												
PbVan												
In (Indicated If observed)												
Se (Indicated If observed)	Se						In					
Total Particles Counted	158			8			107			231		

*Location: P= Plant, R= Residential and C= Commercial

Table 4. Summary of Speciation Results from the Globeville Area.

Sample	45F23Dup 609630			45G08Dup 609631			GV-5			S0-1		
Location*	R			R			R			R		
As (ppm)	524			516			47			107		
	Freq%	RM%	Min-ppm	Freq%	RM%	Min-ppm	Freq%	RM%	Min-ppm	Freq%	RM%	Min-ppm
Slag				3.5%	0.1%	0.5	68.1%	4.2%	1.9			
Clays				2.1%	0.1%	0.5						
Fe Oxide	27.6%	15.5%	81.2	38.5%	6.8%	35.1	4.2%	2.8%	1.3	15.7%	5.8%	6.2
PbSiO4												
Phosphate	29.7%	13.6%	71.2	13.5%	1.9%	9.8				63.7%	19.1%	20.4
As2O3	2.6%	44.6%	233.7	14.5%	76.6%	395.2	4.2%	83.7%	39.3			
AsSbO												
Mn Oxide	34.1%	11.5%	60.2	9.1%	1.0%	5.1	23.6%	9.3%	4.4			
PbAsO	2.1%	14.8%	77.5	6.1%	13.5%	69.6				12.7%	58.9%	63.0
AsCdO												
Cerussite												
Galena												
PbMO										7.8%	16.3%	17.4
PbO				0.7%	0.1%	0.4						
Solder				3.0%	0.0%							
Fe Sulfate												
AsMO												
CaAsO												
Pb												
Gypsum												
Anglesite												
PbCl4												
AlAsO												
Aspy												
AsFeO												
Paint	3.9%			9.0%								
SS												
CdO												
PbVan												
In (Indicated If observed)	In			In						In		
Se (Indicated If observed)												
Total Particles Counted	42			121			6			22		

*Location: P= Plant, R= Residential and C= Commercial

Table 4. Summary of Speciation Results from the Globeville Area.

Sample	SO-7			SO-10			SO-13			SO-14		
Location*	R			R			R			R		
As (ppm)	93			118			63			75		
	Freq%	RM%	Min-ppm	Freq%	RM%	Min-ppm	Freq%	RM%	Min-ppm	Freq%	RM%	Min-ppm
Slag				0.75	0.035439808	4.2	60.7%	12.5%	7.9	57.9%	5.1%	3.8
Clays												
Fe Oxide							15.6%	34.2%	21.5	18.6%	17.4%	13.0
PbSiO4				3.6%			0.6%					
Phosphate	78.7%	27.9%	26.0	10.0%	4.1%	4.8	19.0%	34.0%	21.4	13.2%	10.1%	7.5
As2O3	5.2%	67.9%	63.1	6.1%	92.3%	108.9				2.1%	58.3%	43.7
AsSbO												
Mn Oxide	16.1%	4.2%	3.9									
PbAsO												
AsCdO												
Cerussite												
Galena										3.7%		
PbMO							1.6%	19.2%	12.1	1.2%	6.5%	4.9
PbO												
Solder				5.4%	0.0%	0.1	2.5%	0.1%	0.1			
Fe Sulfate										3.3%	2.6%	1.9
AsMO												
CaAsO												
Pb												
Gypsum												
Anglesite												
PbCl4												
AlAsO												
Aspy												
AsFeO												
Paint												
SS												
CdO												
PbVan												
In (Indicated If observed)				In			In					
Se (Indicated If observed)												
Total Particles Counted	5			10			17			15		

*Location: P= Plant, R= Residential and C= Commercial

Table 4. Summary of Speciation Results from the Globeville Area.

Sample	SO-22			4422 Delaware-F			4425 Pennsylvania-F			4428 Lincoln-F		
Location*	R			R			R			R		
As (ppm)	55			136			43			459		
	Freq%	RM%	Min-ppm	Freq%	RM%	Min-ppm	Freq%	RM%	Min-ppm	Freq%	RM%	Min-ppm
Slag										13.3%	0.2%	1.1
Clays				1.1%	0.2%	0.3						
Fe Oxide				61.5%	41.1%	55.9	73.5%	74.7%	32.0	45.2%	8.8%	40.3
PbSiO ₄										1.1%		
Phosphate				1.5%	0.8%	1.1	23.5%	19.5%	8.3	3.7%	0.6%	2.7
As ₂ O ₃	53.3%	83.9%	46.2							13.7%	80.5%	369.6
AsSbO										1.6%	7.5%	34.2
Mn Oxide				5.7%	2.3%	3.1				20.9%	2.4%	11.1
PbAsO												
AsCdO												
Cerussite				2.9%						0.4%		
Galena												
PbMO	33.3%	9.8%	5.4	0.9%	3.2%	4.4	1.0%	5.8%	2.5			
PbO												
Solder												
Fe Sulfate												
AsMO												
CaAsO				0.064638783	0.523779267	71.2						
Pb												
Gypsum												
Anglesite												
PbCl ₄												
AlAsO												
Aspy												
AsFeO												
Paint				20.0%								
SS	13.3%	6.3%	3.5									
CdO		0.0%	0.0									
PbVan		0	0.0				0.020408					
In (Indicated If observed)							In			In		
Se (Indicated If observed)												
Total Particles Counted	6			31			13			54		

*Location: P= Plant, R= Residential and C= Commercial

Table 4. Summary of Speciation Results from the Globeville Area.

Sample	4438 Lincoln-F			4460 Pennsylvania-F			4460 Pennsylvania-R		
Location*	R			R			R		
As (ppm)	2200			200			441		
	Freq%	RM%	Min-ppm	Freq%	RM%	Min-ppm	Freq%	RM%	Min-ppm
Slag				17.7%	0.3%	0.6			
Clays									
Fe Oxide	6.9%	0.3%	6.7	2.0%	0.3%	0.7	33.9%	3.9%	17.3
PbSiO ₄							8.2%		
Phosphate	3.9%	0.1%	3.1	2.8%	0.4%	0.8	10.1%	0.9%	4.2
As ₂ O ₃	68.6%	91.6%	2014.5	17.8%	89.5%	178.9	25.8%	90.3%	398.2
AsSbO	5.0%	5.3%	116.1	2.0%	8.1%	16.2			
Mn Oxide	5.9%	0.2%	3.4	3.9%	0.4%	0.8	19.7%	1.4%	6.0
PbAsO							0.3%	0.5%	2.1
AsCdO				0.5%	1.0%	2.1			
Cerussite							0.3%		
Galena				0.7%					
PbMO	8.1%	2.0%	44.5						
PbO									
Solder				2.1%	0.0%				
Fe Sulfate	0.6%	0.0%	0.5				0.3%	0.0%	0.1
AsMO									
CaAsO	0.9%	0.5%	11.2						
Pb									
Gypsum									
Anglesite									
PbCl ₄									
AlAsO				0.7%	0.0%	0.0			
Aspy							0.4%	1.5%	6.7
AsFeO							0.9%	1.4%	6.3
Paint				49.5%					
SS									
CdO									
PbVan									
In (Indicated if observed)				In					
Se (Indicated if observed)									
Total Particles Counted	219			56			54		

*Location: P= Plant, R= Residential and C= Commercial

Table 4. Summary of Speciation Results from the Globeville Area.

Sample	49N10012 610806			53R18179 609808			45J200 609620			MO2A 609623		
Location*	R			R			R			P		
As (ppm)	800			402			1348			14		
	Freq%	RM%	Min-ppm	Freq%	RM%	Min-ppm	Freq%	RM%	Min-ppm	Freq%	RM%	Min-ppm
Slag				11.8%	0.6%	2.3						
Clays												
Fe Oxide	32.1%	4.0%	32.3	24.6%	12.5%	50.1	13.9%	1.0%	12.9	37.0%	47.4%	6.6
PbSiO ₄				1.8%			2.8%					
Phosphate	7.5%	0.8%	6.2	0.7%	0.3%	1.2	8.2%	0.5%	6.3	10.0%	10.4%	1.5
As ₂ O ₃	9.1%	34.4%	275.1				45.1%	94.0%	1266.9			
AsSbO	4.0%	12.2%	97.1				0.7%	1.1%	14.6			
Mn Oxide	12.8%	1.0%	7.7	41.2%	12.5%	50.2	26.0%	1.1%	14.4	35.5%	27.3%	3.8
PbAsO	28.9%	45.7%	365.2	1.3%	8.4%	33.7	1.4%	1.2%	16.4			
AsCdO				0.5%	3.1%	12.6						
Cerussite												
Galena										1.9%		
PbMO	0.8%	0.5%	4.3	9.7%	27.7%	111.3	1.1%	0.4%	5.9			
PbO							0.1%	0.0%	0.1			
Solder												
Fe Sulfate	4.2%	0.4%	3.5	1.0%	0.4%	1.8				13.7%	14.9%	2.1
AsMO				3.0%	20.3%	81.5						
CaAsO				1.4%	8.5%	34.2						
Pb												
Gypsum												
Anglesite	0.4%			2.6%						1.9%		
PbCl ₄												
AlAsO												
Aspy	0.3%	0.9%	7.6	0.3%	5.3%	21.2	0.4%	0.8%	10.5			
AsFeO				0.1%	0.5%	2.0						
Paint												
SS												
CdO												
PbVan												
In (Indicated If observed)							In					
Se (Indicated If observed)												
Total Particles Counted	122			78			98			18		

*Location: P= Plant, R= Residential and C= Commercial

Table 4. Summary of Speciation Results from the Globeville Area.

Sample	GV-4			SO-15			SO-16			SO-10		
Location*	R			R			R			R		
As (ppm)	779			1800			30			118		
	Freq%	RM%	Min-ppm	Freq%	RM%	Min-ppm	Freq%	RM%	Min-ppm	Freq%	RM%	Min-ppm
Slag				3.0%	0.0%	0.3						
Clays												
Fe Oxide	31.6%	4.0%	31.5	31.2%	2.0%	36.0	32.0%	25.1%	7.5	44.1%	8.9%	10.5
PbSiO ₄												
Phosphate	8.0%	0.8%	6.5	10.7%	0.6%	10.0	47.1%	30.1%	9.0	42.2%	7.0%	8.2
As ₂ O ₃	22.0%	85.1%	662.6	44.8%	86.7%	1559.9				13.8%	84.1%	99.3
AsSbO				3.3%	5.1%	91.9	1.3%	24.2%	7.3			
Mn Oxide	22.0%	1.7%	13.1				9.6%	4.5%	1.3			
PbAsO	2.6%	4.2%	32.9	7.0%	5.7%	101.9	0.4%	3.6%	1.1			
AsCdO												
Cerussite												
Galena	0.1%											
PbMO	0.9%	0.7%	5.2				1.7%	7.3%	2.2			
PbO	0.4%	0.0%	0.3									
Solder	0.1%	0.0%	0.0									
Fe Sulfate	1.4%	0.2%	1.2				7.9%	5.2%	1.6			
AsMO												
CaAsO	2.1%	3.3%	25.7		0							
Pb	0.1%											
Gypsum												
Anglesite	0.9%											
PbCl ₄												
AlAsO												
Aspy												
AsFeO												
Paint	7.8%											
SS												
CdO												
PbVan												
In (Indicated If observed)												
Se (Indicated If observed)												
Total Particles Counted	135			162			95			26		

*Location: P= Plant, R= Residential and C= Commercial

Table 4. Summary of Speciation Results from the Globeville Area.

Sample	770			9190			9232			9742		
Location*	R			C			C			C		
As (ppm)	181			116			103			168		
	Freq%	RM%	Min-ppm	Freq%	RM%	Min-ppm	Freq%	RM%	Min-ppm	Freq%	RM%	Min-ppm
Slag												
Clays							0.4%	0.1%	0.1			
Fe Oxide	69.8%	35.1%	63.5	81.8%	68.7%	79.7	43.2%	18.1%	18.6	64.8%	74.5%	125.2
PbSiO ₄							1.8%					
Phosphate	2.1%	0.9%	1.6	3.0%	2.1%	2.4	18.8%	6.4%	6.6	27.0%	25.3%	42.5
As ₂ O ₃												
AsSbO												
Mn Oxide	18.4%	5.5%	10.0		0.0%	0.0	0.5%	0.1%	0.1			
PbAsO				1.8%	19.2%	22.2						
AsCdO												
Cerussite												
Galena												
PbMO	4.5%	12.8%	23.2	2.1%	10.0%	11.6	31.9%	75.3%	77.6			
PbO												
Solder										8.2%	0.2%	0.3
Fe Sulfate												
AsMO												
CaAsO												
Pb												
Gypsum												
Anglesite												
PbCl ₄												
AlAsO												
Aspy	1.1%	17.0%	30.8									
AsFeO	4.0%	28.7%	52.0									
Paint							3.4%					
SS												
CdO				11.2%								
PbVan												
In (Indicated If observed)												
Se (Indicated If observed)												
Total Particles Counted	73			17			47			43		

*Location: P= Plant, R= Residential and C= Commercial

Table 4. Summary of Speciation Results from the Globeville Area.

Sample	9779			71		
Location*	C			R		
As (ppm)	146			170		
	Freq%	RM%	Min-ppm	Freq%	RM%	Min-ppm
Slag						
Clays						
Fe Oxide	92.9%	97.6%	142.5	36.7%	9.0%	15.3
PbSiO ₄						
Phosphate	2.6%	2.2%	3.2	45.3%	9.1%	15.4
As ₂ O ₃				10.1%	74.8%	127.2
AsSbO						
Mn Oxide				1.4%	0.2%	0.4
PbAsO				1.9%	5.9%	10.1
AsCdO						
Cerussite						
Galena						
PbMO						
PbO				1.7%	0.3%	0.5
Solder	3.8%	0.1%	0.1			
Fe Sulfate	0.1%	0.1%	0.1	2.9%	0.6%	1.0
AsMO						
CaAsO						
Pb						
Gypsum						
Anglesite						
PbCl ₄						
AlAsO						
Aspy						
AsFeO						
Paint						
SS						
CdO						
PbVan						
In (Indicated If observed)						
Se (Indicated If observed)						
Total Particles Counted	54			36		

*Location: P= Plant, R= Residential and C= Commercial

Equation 1.0 will serve as an example of how to calculate the frequency of occurrence for an arsenic-bearing compound.

F_{As} - Frequency of occurrence of arsenic
in a single phase.

PLD - An individual particle's longest
dimension

$$F_{As} \text{ in phase-1} = \frac{\sum (PLD)_{\text{phase-1}}}{\sum (PLD)_{\text{phase-1}} + \sum (PLD)_{\text{phase-2}} + \sum (PLD)_{\text{phase-n}}} \quad \text{Eq. 1.0}$$

$$\%F_{As} \text{ in phase-1} = F_{As} \text{ in phase-1} * 100$$

Thus, the frequency of occurrence of arsenic in each phase (F_{As}) is calculated by summing the longest dimension of all particles observed for that phase and then dividing each phase by the total of the longest dimensions for all phases. The data generated thus illustrate which arsenic-bearing phase(s) are the most commonly observed in the sample or relative volume percent.

The second calculation used in this report determines the RELATIVE MASS ARSENIC (RM_{As}) in a phase. These data are calculated by substituting the PLD term in the equation above with the value of M_{As} . This term is calculated as defined below.

M_{As} - Mass of arsenic in a phase

SG - Specific Gravity of a phase

ppm_{As} - Concentration in ppm of arsenic
in phase (see Table A6.0, Appendix II)

$$M_{As} = F_{As} * SG * ppm_{As} \quad \text{Eq. 2.0}$$

The advantage in reviewing the RELATIVE MASS ARSENIC determinations is that it gives one information as to which metal-bearing phase(s) in a sample is likely to control the total bulk concentration for arsenic. As an example, PHASE-1 may, by relative volume, contribute 98% of the sample, however it has a low specific gravity and contains only 1000 ppm arsenic, whereas PHASE-2 contributes 2% of the sample, has a high specific gravity and contains 85,000 ppm of arsenic. In this example it is PHASE-2 that is the dominant source of arsenic to the sample.

The third calculation is to determine the MINERAL MASS ARSENIC (Min_{As}). In this calculation the RM_{As} is simply multiplied by the bulk concentration of arsenic found in the sample:

$$Min_{As} = RM_{As} * As_{Bulk} \quad \text{Eq. 3.0}$$

Where As_{Bulk} is the bulk arsenic for the sample speciated. These values are most useful for geostatistical calculations, such as kriging, or apportionment since values are not forced to 100%.

4.1.1 Point Counting

Counts are made by traversing each sample from left-to-right and top-to-bottom. The amount of vertical movement for each traverse would depend on magnification and CRT (cathode-ray tube) size. This movement should be minimized so that NO portion of the sample is missed when the end of a traverse is reached. Two magnification settings should be used, one ranging from 40 to 100X and a second from 300 to 600X. The last setting will allow one to find the smallest identifiable (1-2 micron) phases.

The portion of the sample examined in the second pass, under the higher magnification, will depend on the time available, the number of arsenic-bearing particles, and the complexity of metal mineralogy. A maximum of 8 hours will be spent per sample.

4.1.2 Precision and Accuracy

The precision of the EMPA speciation is determined based on sample duplicates run every 20 samples. These data will be made available upon request from CDPHE. The accuracy of an analysis is estimated from a statistical evaluation of point counting data based on the method of Mosimann (1965).

4.2 Plant Soils

During the 110 year operational history of the Globe/ASARCO facility, numerous sources of heavy-metal, fugitive emissions existed, including:

Roasters

Arsenic kitchens

Storage piles

Plant road dust

Loading/unloading facilities

Sediment ponds

Baghouses/dust collectors

Few of these sources are available today for sampling, therefore, plant-site samples were limited to the Godfrey stack, the sediment pond, and soils near the Godfrey roaster (fallout). In terms of the historical speciation of arsenic at the plant, these samples are most certainly incomplete and potentially misleading, as the plant soils have been highly disturbed during the plant operation. Thus these samples provide only a partial "source fingerprint." Some specific reasons include:

- Soils were moved and turned repeatedly when drainage patterns were altered, ditches were created and/or filled, buildings were demolished and roadways established and/or paved. The former sedimentation pond was filled, and a neutralization pond created and now covered.

- Material from the present Godfrey stack represents only the most recent roasting history of the facility, while arsenic was primarily roasted in facilities long since demolished or moved.
- Shallow samples (< 12") were collected from the sediment pond, and therefore represent only the most recent activities.
- Soils within a few hundred feet of the stack fall within an "emission shadow" and likely are depleted in phases from the most volatile metals, i.e., arsenic indium, and antimony.
- Historically, arsenic trioxide was the dominant form of arsenic produced at the plant.

Plant samples studied to date have arsenic masses dominated (90% of the relative arsenic mass) by the following arsenic-bearing phases: AsMO , CaAsO , PbAsO , and As_2O_3 (Figure 2, Photos 1 and 2). The most common metals "M" are Ca, As, Pb, Sb, or Cd. Particle size of arsenic phases are bimodal in their distribution with populations at 5 microns and 100+ microns (Figure 3). The 5 micron population is dominated by both AsMO and PbAsO , whereas the coarser, 100+ micron population contains AsMO , As_2O_3 , FeAsO , and CaAsO (Figures 4-5). These latter two phases have a distinctive, coarse grain-size distribution.

Globeville, CO

ASARCO Globe Plant Site

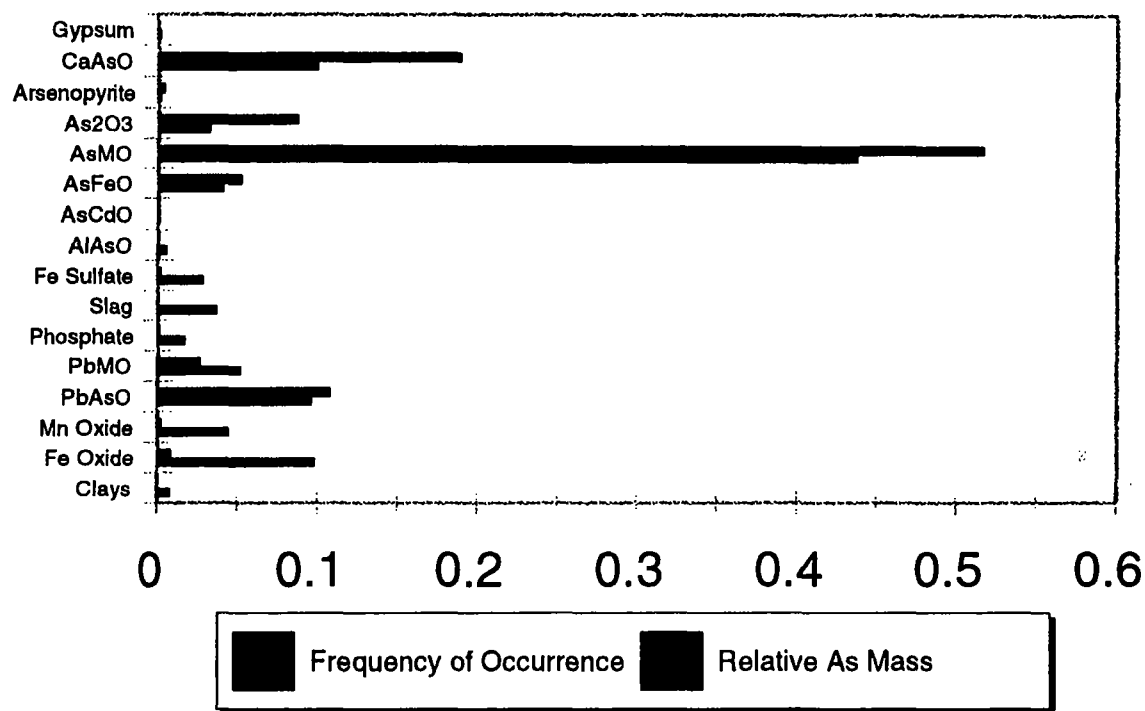


Figure 2. Summary Arsenic Speciation from ASARCO Globe Plant Samples.

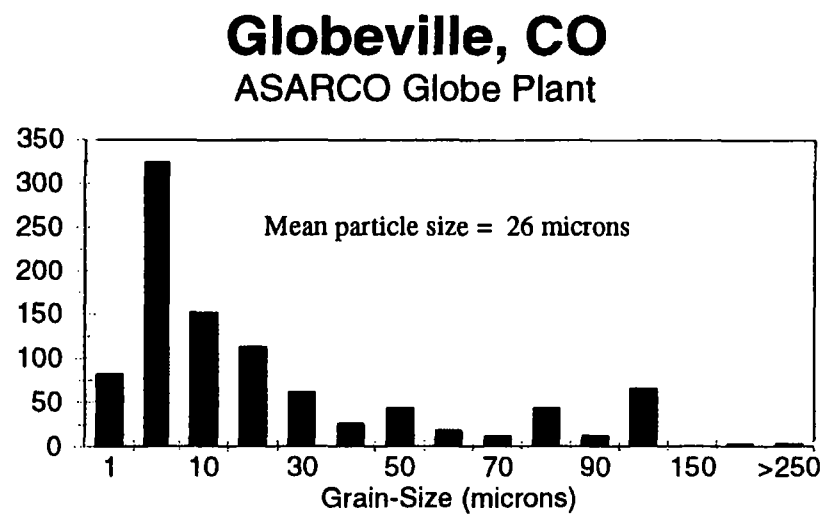


Figure 3. Grain-Size Distribution of Arsenic-Bearing Particles in Globe Plant Soils.

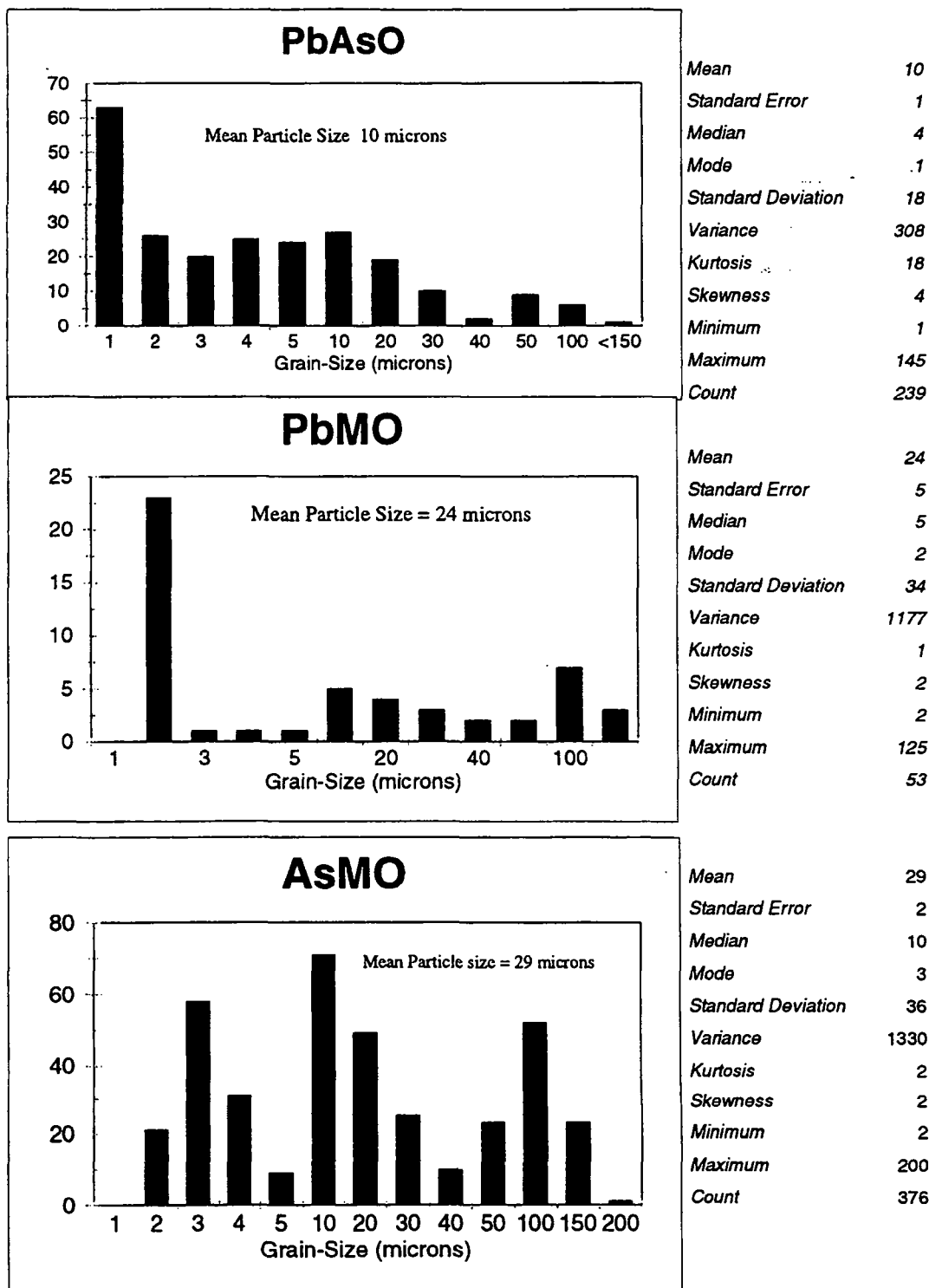


Figure 4. Particle-size Distribution for Dominant Arsenic Phases from Plant.

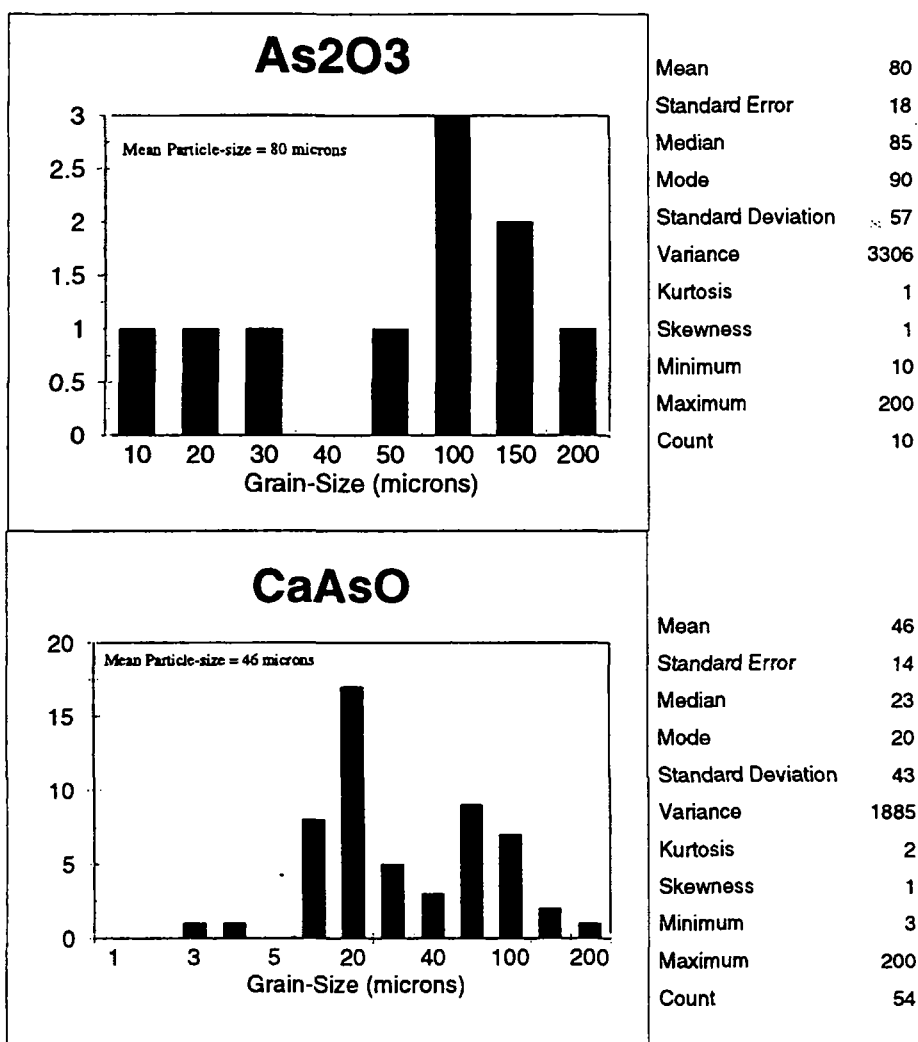


Figure 5. Particle-size Distribution of Dominant Arsenic Phases from Plant.

Each of the sampled media show unique arsenic speciation. Sediment pond samples are dominated by AsMO and CaAsO, and are the only media collected on the site to contain As₂O₃. Godfrey roaster samples are dominated by AsMO, whereas stack fallout is characterized again by AsMO along with typical “soil interacting” phases: Mn oxide, Fe oxide, and phosphate. These phases are the result of soluble arsenic sorbing onto Mn, Fe, and/or P minerals that are commonly found in soils.

In addition to the arsenic species identified in the plant-site sample set, other heavy metal species, consistent with Globe/ASARCO production, were identified. These include In-metal, Se-Hg and Se-Tl compounds, Cd-metal, CdO, CdCl₄, PbO, Pb-metal, PbSO₄, PbS, and PbCO₃ (Photo 3).

4.3 Community Soils

The study was initiated when anomalously high, bulk arsenic concentrations along the southernmost sampling grid of the Globeville site, near I-70, were identified. The community soil sample set (Figure 1) includes soils with varied bulk arsenic concentrations (30 -3873 mg/kg). These samples have arsenic masses almost exclusively (80% of the relative arsenic mass) dominated by As₂O₃, with minor contributions from other arsenic forms (Figure 6). The particle-size distribution for all arsenic species is unimodal, at approximately 11 microns (Figure 7). The As₂O₃ particles are smaller, and generally liberated (Photos 4-7) with a median particle size of 6 microns (Figure 9). The As₂O₃ is of a very pure nature, with only trace quantities of

other metals (< 100 ppm Sb, Cd, or Ca). This chemistry is much more consistent with that of a “product” than that of a stack emission. The morphology of the larger As_2O_3 particles (euhedral to subhedral crystals, Photo 7) is distinctly different than what one finds in emission products (small, round “blebs”, Photo 8), supporting this conclusion.

Globeville, CO

Community Soils

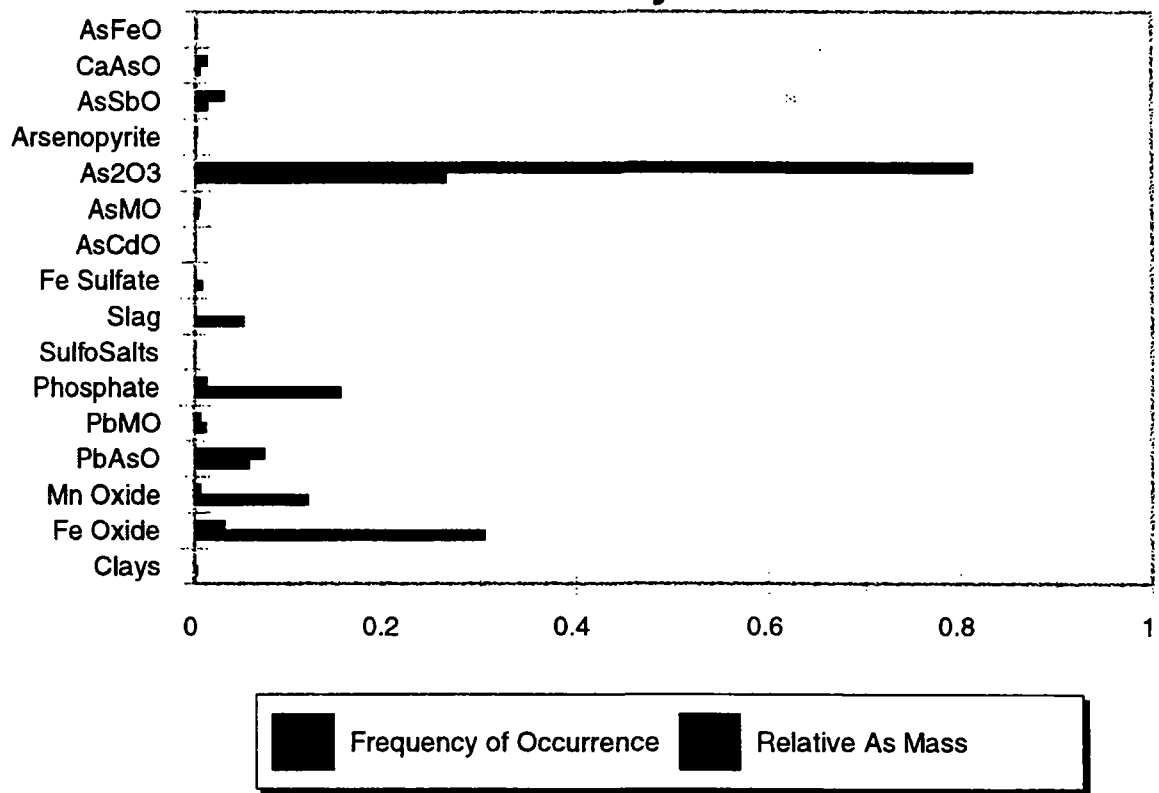


Figure 6. Summary Arsenic Speciation from Globeville Community Soils.

Globeville, CO

Community Soils

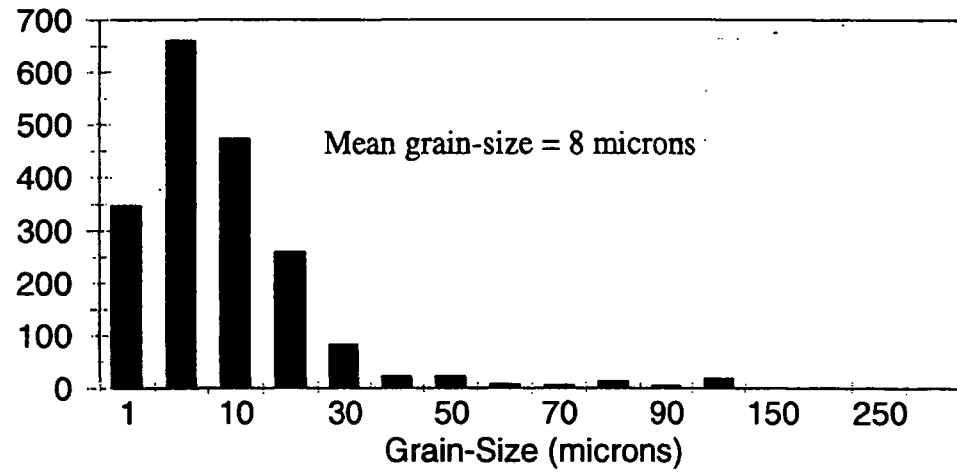
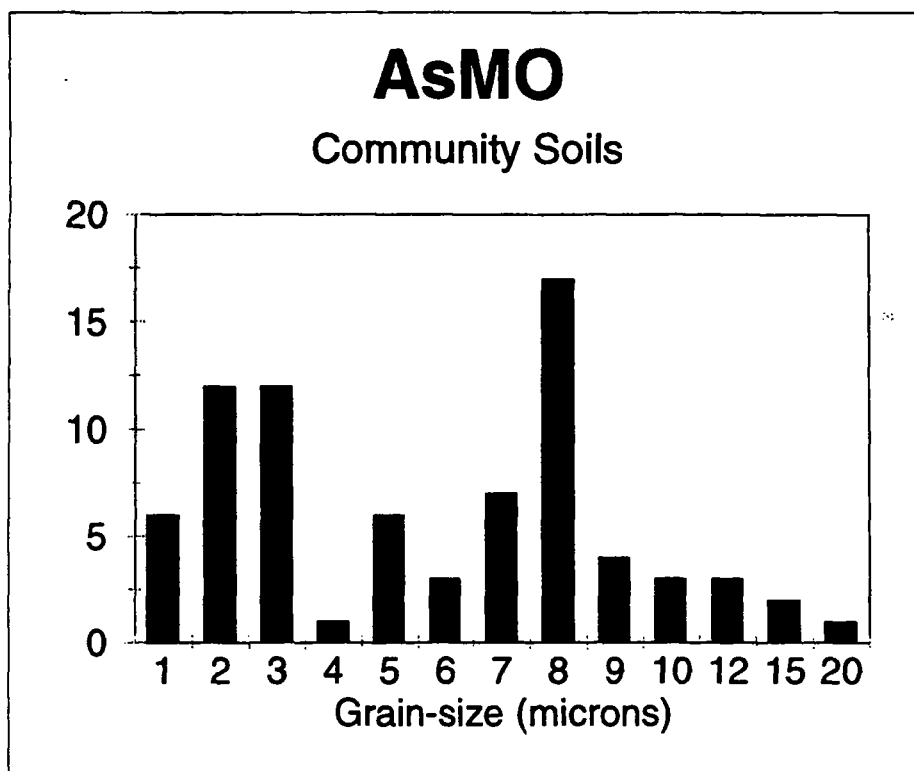
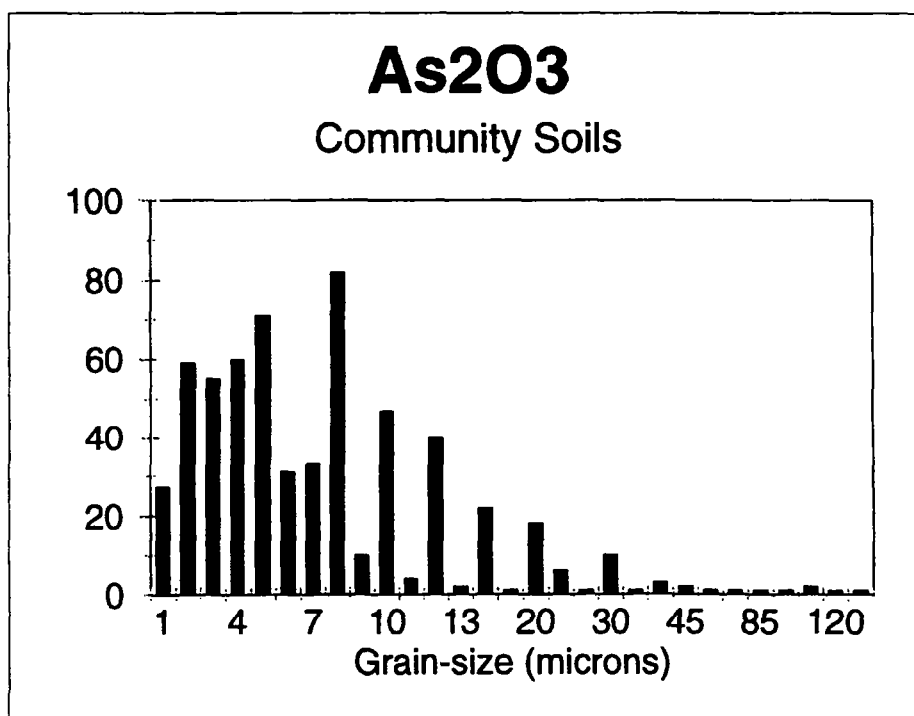


Figure 7. Grain-Size Distribution of Arsenic -Bearing Particles in Community Soils.



Mean	6.5
Standard Error	0.5
Median	7.0
Mode	8.0
Standard Deviation	4.0
Variance	15.6
Kurtosis	1.5
Skewness	1.0
Minimum	1.0
Maximum	20.0
Count	54.0



Mean	9.1
Standard Error	0.6
Median	6.0
Mode	8.0
Standard Deviation	13.8
Variance	190.8
Kurtosis	79.0
Skewness	7.6
Minimum	1.0
Maximum	200.0
Count	592.0

Figure 8. Grain-Size Distribution for AsMO and As2O3 in Community Soils.

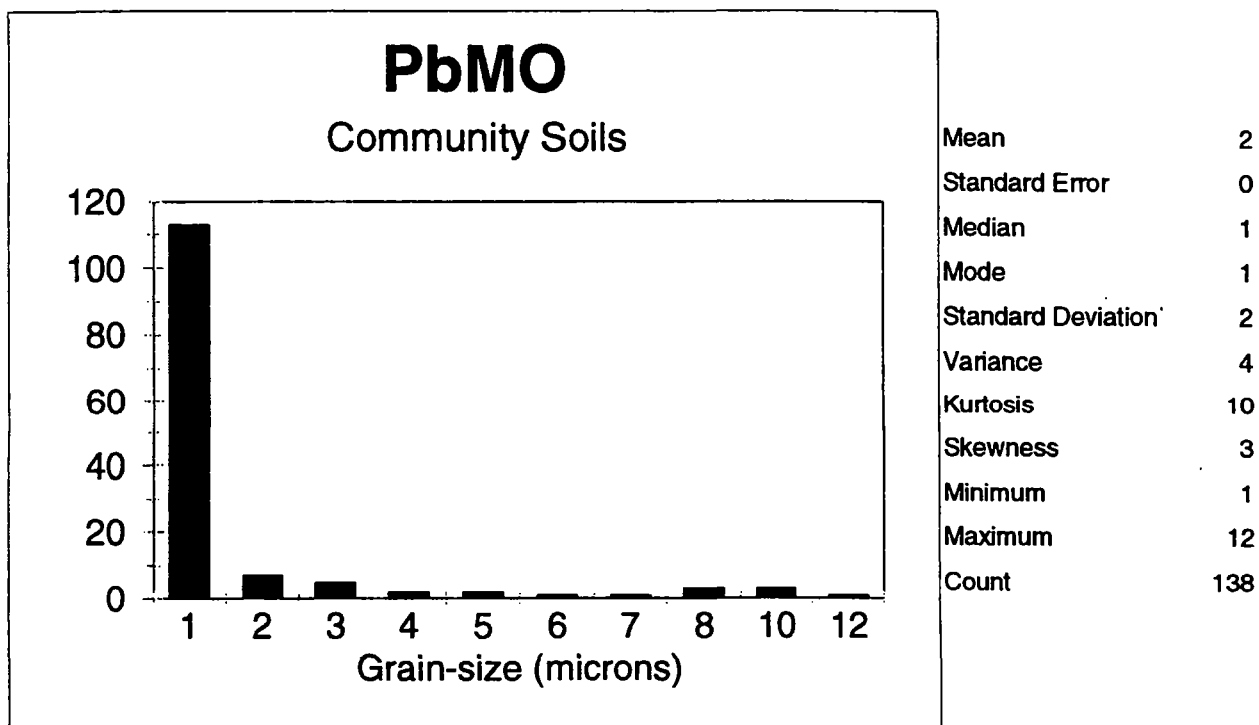
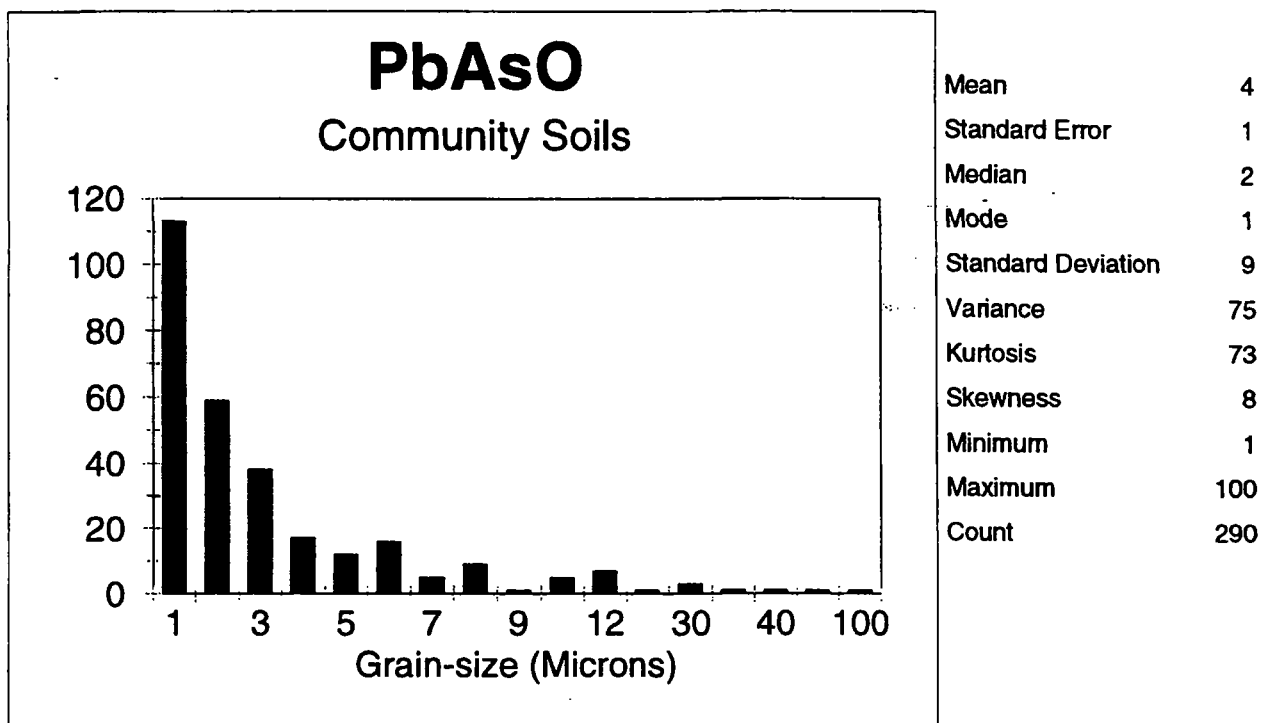


Figure 9. Grain-size Distribution of PbAsO and PbMO in Community Soils.

Although As_2O_3 is the predominant form of arsenic in these samples, all samples contain other forms [PbAsO , AsMO , (M indicates minor concentrations of Sb, Ca, Pb, and/or Cd) and CaAsO], Photos 8-10, which become volumetrically significant in some yards (6090606, 6090617, and 6090630, Table 4), and their presence is not indicative of pesticides as a source for at least a portion of the arsenic. Since neither party was able to obtain a sample of PAX, we speciated both a commercial pesticide (ACME brand) and orchard soils contaminated with arsenical pesticide, and found none of these other arsenic-bearing forms (AsMO , CaAsO , or PbMO) (supporting information will be made available upon request from CDPHE). Again, community soils contain non-arsenic-bearing phases: In-metal, slag, and Se-Tl-Hg (Photos 11-13). Some of these metals (In, Se, Hg, and Tl) have very low crustal abundances;

Crustal Abundance (Rose et al., 1979)

In = 0.1 mg/kg
Se = 0.1 mg/kg
Hg = 0.02 mg/kg
Tl = 0.45 mg/kg

and are likely to be measurable only when associated with pyrometallurgical processes, where the metals are enriched through repeated recirculation of baghouse dusts such as occurred at the Globe plant. Although other area smelters may have contributed much smaller amounts, the Globe facility was designed for the recovery of these "specialty metals" and received enriched baghouse dusts specifically for the purpose of their recovery. Furthermore, the concentrates smelted at such a facility would have to be enriched in In-Se-Tl-Hg in order for these metals to be found in area soils. Based on the author's experience in speciation of soils from numerous smelter facilities, including Leadville, CO, Anaconda, MT, Butte, MT, Midvale, UT, Murray,

UT, Sandy, UT, Tacoma, WA, Palmerton, NJ, Tri-State, OK, this situation is uncommon, and the frequency of these occurrences at the Globe site has no precedence.

The predominance of As_2O_3 is not limited to soils with anomalously high bulk arsenic content. Yards with relatively low arsenic contents (SO-7, SO-10, SO-14, SO-22, and GV-5) still contain significant As_2O_3 (Figure 10, pocket) with no other arsenic-bearing form dominating arsenic “relative mass.”

4.4 Statistical Study--Factor Analysis

A matrix was constructed using seventeen variables and 33 cases (see Appendix III for listing of samples used in matrix) to conduct a factor analysis using *STATISTICA*. The variables included data from the Globeville speciation study (F_{As}), bulk metals concentrations, and information on case locations (plant or residential), Table 4. Based on these data a correlation matrix was computed. The most significant correlations between variable pairs have been marked in red in Table 5. The two observations that one can make from the data, which are most important to this study, are the highly significant ($r = 0.66$, $p < 0.05$) correlation between As_2O_3 and AsSbO and the total lack ($r = -0.02$) of a correlation between As_2O_3 and PbAsO . This data is contrary to the argument that the arsenic trioxide found in the community soils is related to either an arsenic pesticide or an arsenic/lead arsenate herbicide (PAX).

To further investigate the above correlations a preliminary factor analysis study was conducted. Five factors were identified in the data set using principal components (the number of factors

selected are determined following the method of Kaiser, 1960 ie. NO eigenvalues < 1.0), accounting for approximately 71% of the variance. The factors represent lines of maximal variance about the data set. Each consecutive factor is defined to maximize the variability not captured by the preceding factor. Factor loadings, Figure 11 and 12, graphically support these conclusions. Arsenic trioxide is co-located with the pyrometallurgical phases AsSbO, sulfosalts, and slag, while lead arsenate is co-located with a different set of pyrometallurgical phases CaAsO, or arsenopyrite.

Table 5. Correlation matrix of Factor Analysis

	Slag	As ₂ O	AsSbO	PbAsO	AsCdO	PbMO	AsMO	CaAsO	AlAsO	Aspy	AsFeO	SS	Se	In	As	Pb	Site
Slag	1.0	-.26	-.17	-.31	-.02	-.16	-.22	-.12	-.08	-.18	-.10	-.09	-.19	.02	-.26	-.12	.03
As ₂ O ₃	-.26	1.0	.66	-.02	-.18	.03	-.22	-.10	-.10	.08	-.11	.38	-.18	-.16	-.09	-.13	-.33
AsSbO	-.17	.66	1.0	.30	-.07	-.09	-.19	-.09	-.01	-.01	-.08	-.08	-.16	-.19	-.07	-.07	-.25
PbAsO	-.31	-.2	.30	1.0	-.14	-.13	.29	.08	.10	.14	.14	-.11	.35	-.17	.30	-.01	.14
AsCdO	-.02	-.18	-.07	-.14	1.0	-.08	-.14	-.08	.02	-.03	-.06	-.06	-.13	-.00	-.16	-.07	.36
PbMO	-.16	.03	-.09	-.13	-.08	1.0	.04	-.08	-.01	-.05	.01	.35	-.09	.07	.35	.87	.21
AsMO	-.22	-.22	-.19	.29	-.14	.04	1.0	.31	.41	.18	.46	-.08	.81	-.11	.70	.02	.50
CaAsO	-.12	-.10	-.09	.08	-.08	-.08	.31	1.0	-.06	-.09	-.05	-.04	.63	.26	.44	-.03	.41
AlAsO	-.08	-.1	-.01	.10	.02	-.01	.41	-.06	1.0	.54	.94	-.04	.43	-.08	.41	-.01	.26
Aspy	-.18	.08	-.01	.14	-.03	-.05	.18	-.09	.54	1.0	.62	-.07	.20	-.19	.18	-.05	.03
AsFeO	-.10	-.11	-.08	-.11	-.06	.35	-.08	-.04	-.04	-.07	1.0	-.03	.47	-.17	.45	0.0	.30
SS	-.09	.38	-.08	-.11	-.06	.35	-.08	-.04	-.04	-.07	-.03	1.0	-.07	.16	-.09	-.04	-.10
Se	-.19	-.18	-.16	.35	-.13	-.09	.81	.63	.43	.20	.47	-.07	1.0	.05	.84	.01	.65
In	.02	-.16	-.19	-.17	-.00	.07	-.11	.26	-.08	-.19	-.17	-.16	.05	1.0	.11	.18	.07
As	-.26	-.09	-.07	.30	-.16	.35	.70	.44	.41	.18	.45	-.09	.84	.11	1.0	.50	.71
Pb	-.12	-.13	-.07	-.01	-.07	.87	.02	-.03	-.01	-.05	0.0	-.04	.01	.18	.50	1.0	.36
Site	.03	-.33	-.25	.14	.36	.21	.50	.41	.26	.03	.30	-.10	.65	.07	.71	.36	1.0

Figure 11. Plot of factor loadings from arsenic speciation factor analysis.

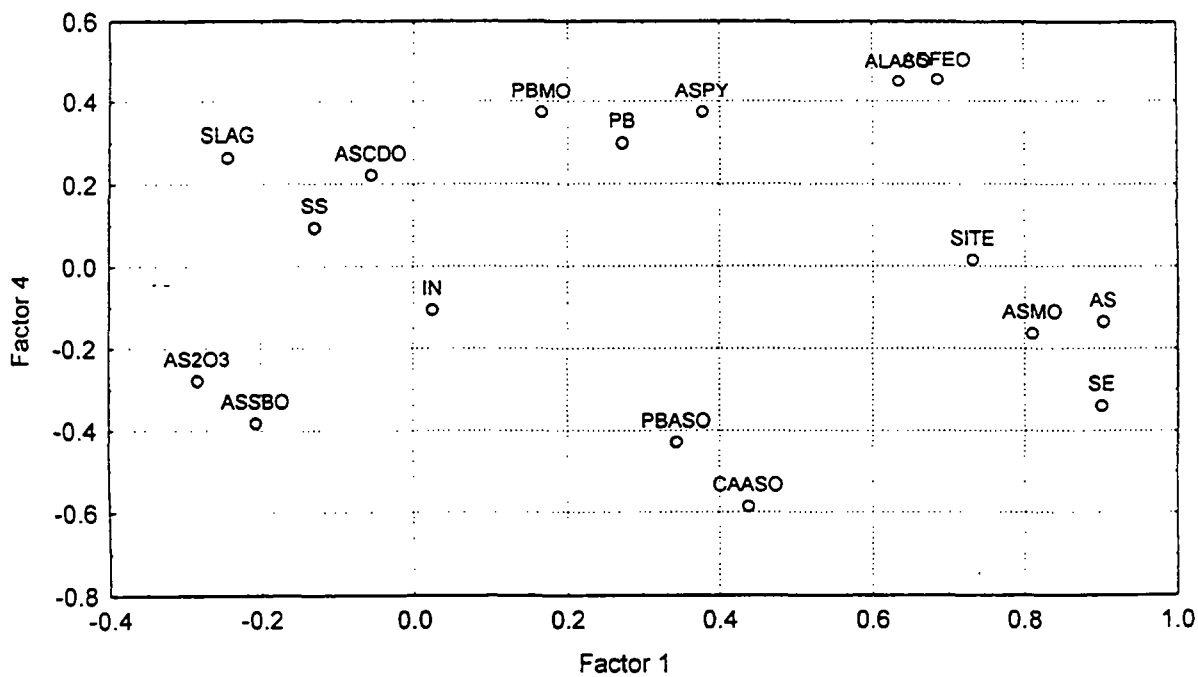
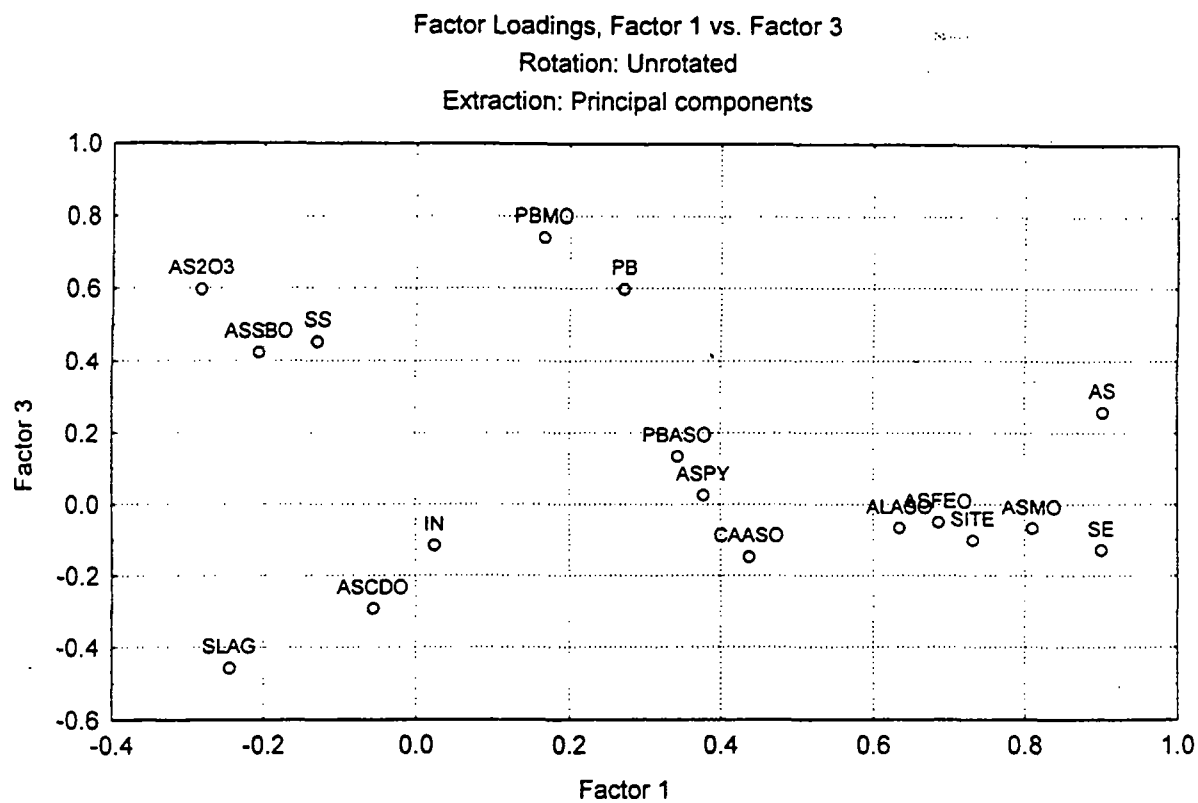
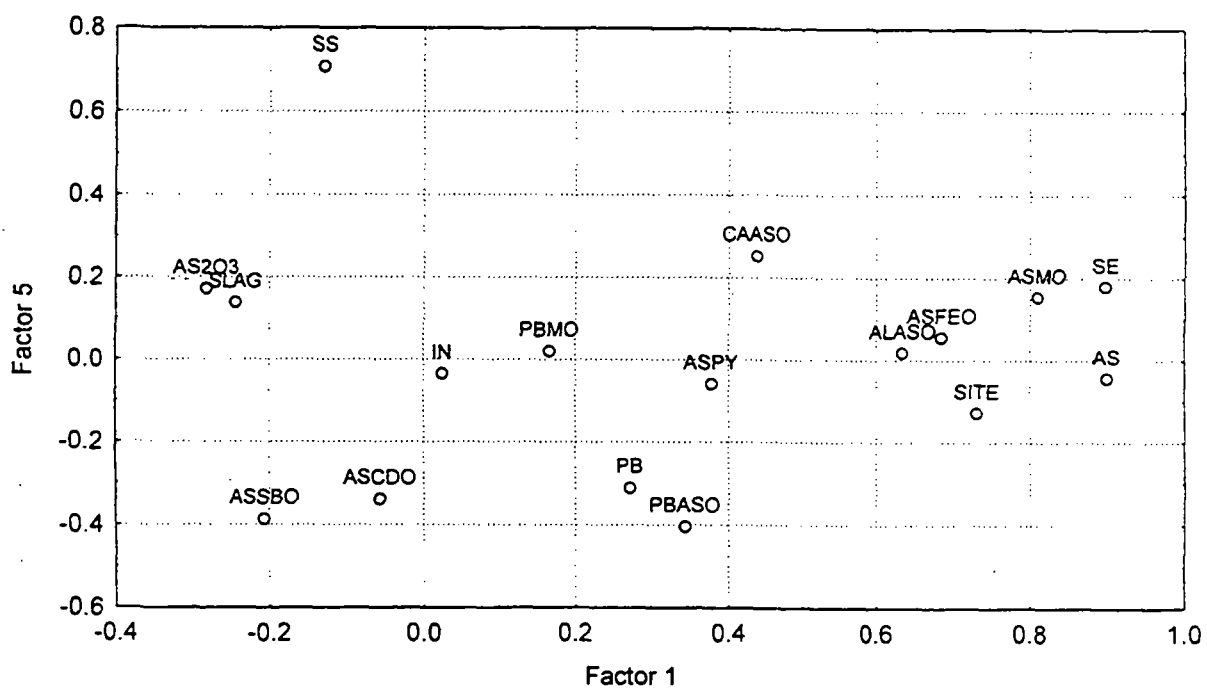
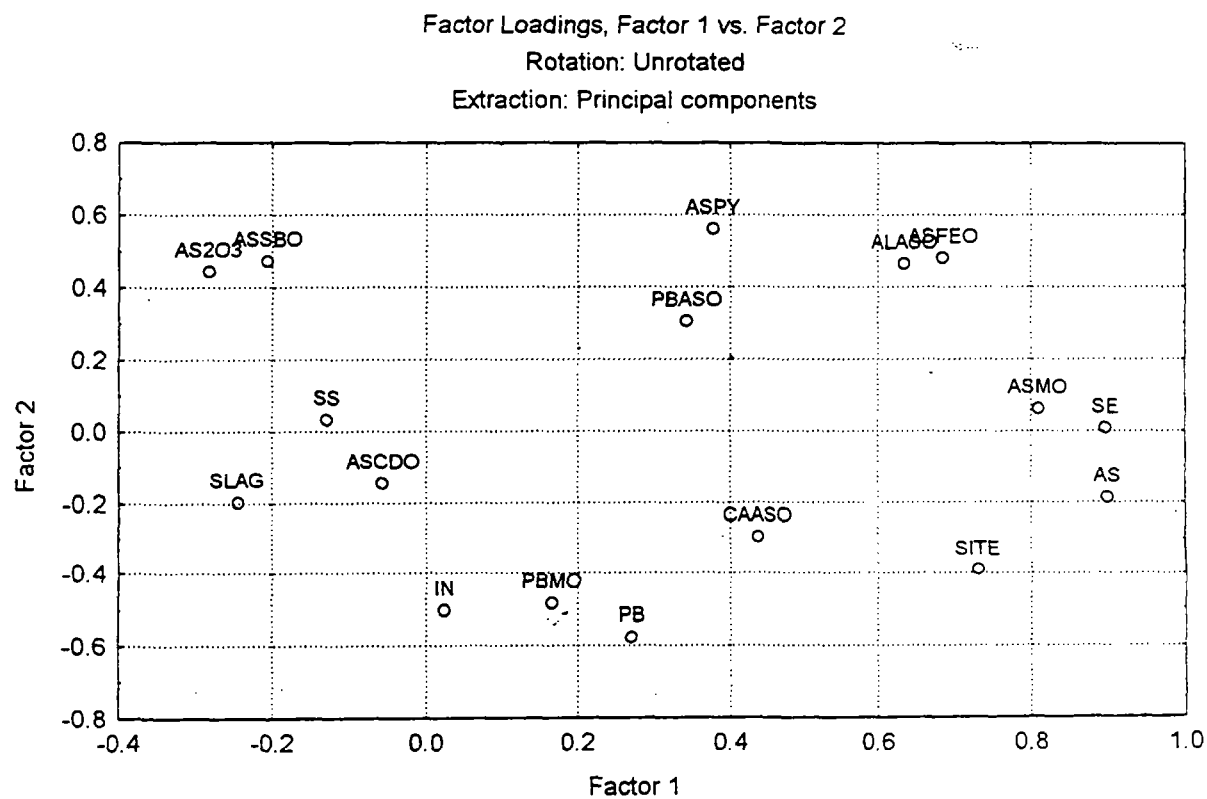


Figure 12. Plot of factor loadings from arsenic speciation factor analysis.



5.0 SOIL COLUMNS

Column experiments were conducted to investigate the leaching potential of As_2O_3 or lead arsenate-bearing herbicides /insecticides when applied to properties in the Globeville area. The leachate of each column, which took about 4 hours to percolate down the column, were collected in a clean 500 ml Nalgene® bottles. The pH and conductivity of all samples were measured. Approximately 15 ml of leachate was filtered ($0.45\ \mu\text{m}$), preserved with two drops of OPTIMA® nitric acid, and then analyzed following EPA Method 600 for arsenic and lead.

The experiments were performed in two stages. In the first stage two application rates (run in duplicate) of PbAsO, the most commonly used compound in herbicides/insecticides during the 1940-1960s, were selected. Each of the columns (24 inches high by 2.5 inches in diameter) was packed with Colorado top soil (Top Choice®), and 10 grams of PbAsO were distributed on top of the soil in Columns G1 and G3, and 0.1 g in Columns G2 and G4. The columns with the 0.1 g of PbAsO are the equivalent of 10 lb/1000 ft² (a normal application would be from 5 to 20 lb/1000 ft²), whereas the columns with 10 g of PbAsO have about 100 times more amendment than the normal application. Each column was then saturated with 1 liter of Boulder tap water, followed by measured aliquots of tap water about every four days. Boulder tap water was used instead of deionized water or a synthetic rain water, as it was assumed that residential watering was the major source of moisture during most of the year. Care was taken in pouring the water into the columns so as to prevent serious disruption of the AsPbO-soil layer on top of the columns.

The data, Figure 13, Table 6, indicate two important facts: 1) soils treated with lead arsenate will release arsenic, leaching out of the A-O horizons, potentially into shallow aquifers; and 2) the lead in soils treated with lead arsenate will not leach, but will remain in the upper few inches of the soil. The result over time of these two processes would be a constant increase in Pb/As ratios in soils treated with lead arsenate. Similar observations have been made by Davenport and Peryea, 1991, Merry et al., 1983, and Peryea, 1989, 1991. Although the leaching of arsenic is not directly proportional to the application rate, it appears that these observations hold true even for very high (> 100 times the normal) application rates.

In the second stage of the study, two columns as above were prepared with 5 g of synthetic PAX (Column A) and 5 g of arsenic trioxide (Column B). Because PAX was not available to our laboratory, a mixture of 25.11% As_2O_3 , 8.25% PbAsO , and 66.64% ground quartz (SiO_2) was prepared in house to represent PAX and used in Column A. This mixture was thought to be chemically similar to PAX, based on available literature on PAX, Hiltbold, 1973. As observed in Stage 1, the lead contents of the leachates of Columns A and B were low (Table 6), whereas considerable amounts of arsenic were leached. Column B leached ~4 times more arsenic than Column A, which is consistent with the increase in bulk arsenic between the two columns.

Table 6. Data from column leaching experiments.

Column 1, 10 g of PbAsO

	pH	Cond. (mS/cm)	Date	As	Pb	Volume added (ml)
1			6/9/97	0.8	0.16	1000
2	7.34	52.0	6/9/97	1.5	0.25	750
3	7.38	30.0	6/13/97	2.0	0.19	750
4	7.69	9.6	6/18/97	4.0	0.13	500
5	7.36	6.9	6/20/97	6.7	0.09	500
6	7.24	5.2	6/23/97	9.5	0.08	500
7	7.27	4.1	6/26/97	10.6	0.09	500
8	7.10	4.1	7/1/97	10.8	0.07	500
9	7.66	3.5	7/7/97	12.4	0.08	500
10	7.19	3.6	7/10/97	14.2	0.10	500
11	7.39	3.3	7/16/97	12.5	0.07	500
12	7.17	3.1	7/18/97	10.6	0.05	500

Column 2, 0.1 g PbAsO

1			6/9/97	0.81	0.16	1000
2	7.40	72.0	6/9/97	1.04	0.14	750
3	7.70	50.0	6/13/97	0.92	0.08	750
4	7.77	10.0	6/18/97	1.73	0.09	500
5	7.49	6.8	6/20/97	2.67	0.07	500
6	7.30	5.2	6/23/97	3.64	0.06	500
7	7.31	4.1	6/26/97	3.73	0.08	500
8	7.32	4.1	7/1/97	3.45	0.06	500
9	7.60	4.4	7/7/97	3.13	0.09	500
10	7.30	3.5	7/10/97	3.38	0.08	500
11	7.55	3.3	7/16/97	1.65	0.06	500
12	7.51	3.2	7/18/97	1.95	0.06	500

Column 3 10 g PbAsO

1			6/9/97	0.904	0.16	1000
2	7.26		6/9/97	3.027	0.49	750
3	7.38		6/13/97	3.625	0.23	750
4	7.60		6/18/97	5.245	0.12	500
5	7.55		6/20/97	8.632	0.16	500
6	7.40		6/23/97	9.599	0.10	500
7	7.30		6/26/97	9.487	0.08	500
8	7.23		7/1/97	11.09	0.08	500
9	7.53		7/7/97	12.636	0.08	500
10	7.21		7/10/97	13.107	0.08	500
11	7.47		7/16/97	12.46	0.06	500
12	7.05		7/18/97	11.089	0.08	500

Column 4, 0.1 g PbAsO

1			6/9/97	0.75	0.15	1000
2	7.40		6/9/97	0.99	0.14	750
3	7.36		6/13/97	0.92	0.11	750
4	7.85		6/18/97	1.76	0.08	500
5	7.49		6/20/97	2.52	0.11	500
6	7.42		6/23/97	3.00	0.06	500
7	7.19		6/26/97	3.31	0.07	500
8	7.13		7/1/97	3.65	0.06	500
9	7.43		7/7/97	3.49	0.08	500
10	7.17		7/10/97	3.75	0.08	500
11	7.46		7/16/97	3.40	0.06	500
12	7.25		7/18/97	3.03	0.05	500

Column A, 5 g syn. PAX

1	7.64	95.2	7/25/97	22.3	0.11	1000
2	7.47	14.5	7/30/97	30.7	0.09	500
3	7.39	8.0	8/1/97	37.5	0.08	500
4	7.75	5.0	8/5/97	32.7	0.06	500
5	7.67	4.4	8/13/97	22.5	0.07	500
6	7.73	3.8	8/18/97	36.9	0.07	500
7	7.55	3.3	8/21/97	40.4	0.09	500
8	7.55	3.3	8/25/97	34.6	0.07	500
9	7.57	3.1	8/28/97	33.8	0.07	500
10	7.59	3.2	9/4/97	27.4	0.07	500

Column B, 5 g As₂O₃

1	7.67	87.3	7/25/97	21.0	0.11	1000
2	7.46	15.4	7/30/97	88.3	0.10	500
3	7.38	8.3	8/1/97	96.3	0.08	500
4	8.04	5.3	8/5/97	108.1	0.05	500
5	7.56	4.2	8/13/97	127.4	0.08	500
6	7.53	3.6	8/18/97	137.7	0.08	500
7	7.46	3.3	8/21/97	133.8	0.07	500
8	7.54	3.3	8/25/97	118.1	0.08	500
9	7.59	3.1	8/28/97	88.4	0.06	500
10	7.40	3.2	9/4/97	88.4	0.07	500

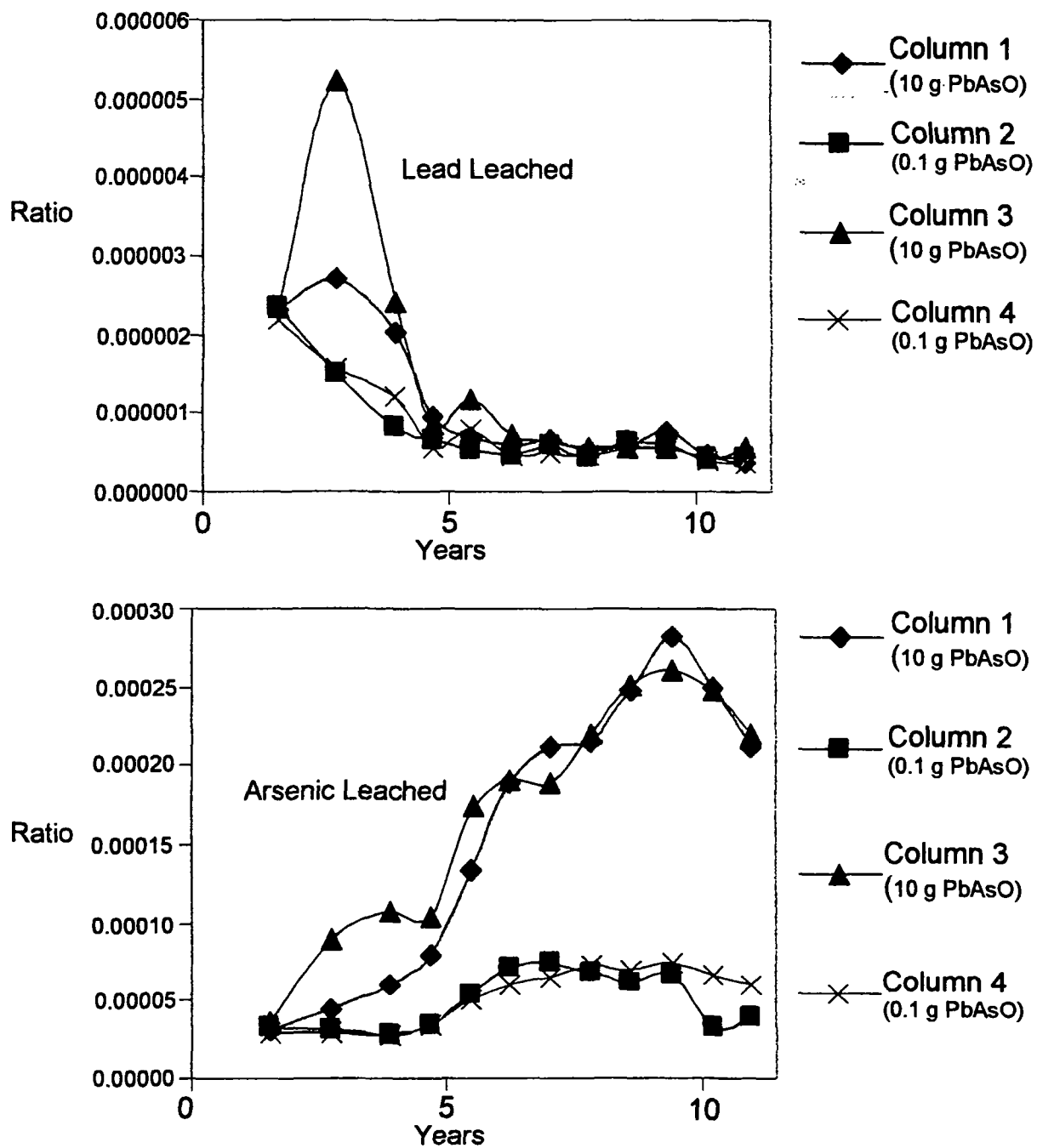


Figure 13. A plot of ratio of lead leached from column to amount of lead added to column versus years of leaching (top). A plot of ratio of arsenic leached from column to amount of arsenic added to column versus years of leaching (bottom). Years calculated by calculating height of leaching solution (volume added divided by area of column) and then dividing height of leaching solution added by average rain fall in Denver Area (31.37 cm/year, National Climate Data Center).

6.0 ARSENIC FROM A PESTICIDE

The results of Column A, which contained 5 grams of synthetic PAX, along with local rainfall measurements were used to model the amount of arsenic and lead that would remain in treated soils after a period of time (Figure 14). Based on the observed data, leaching rates for the two metals were calculated for various pesticide application rates (Figure 15). A flowchart outlining in detail these calculations is included in Appendix II. Figure 14 illustrates the predicted behavior of a normal application (20 lb/1000 ft²) of PAX within the upper 4 inches of soil over time in the Globeville area. To find a soil today with approximately 2300 mg/kg of arsenic (similar to 4438 Lincoln) would have required an initial arsenic concentration of 4300 mg/kg, if applied to the soil approximately 30 years ago (last known production and sale of PAX is 1971). This concentration would represent 54 times the normal, recommended application rate, requiring the landowner to apply nearly 1100 pounds of PAX, Figure 16.

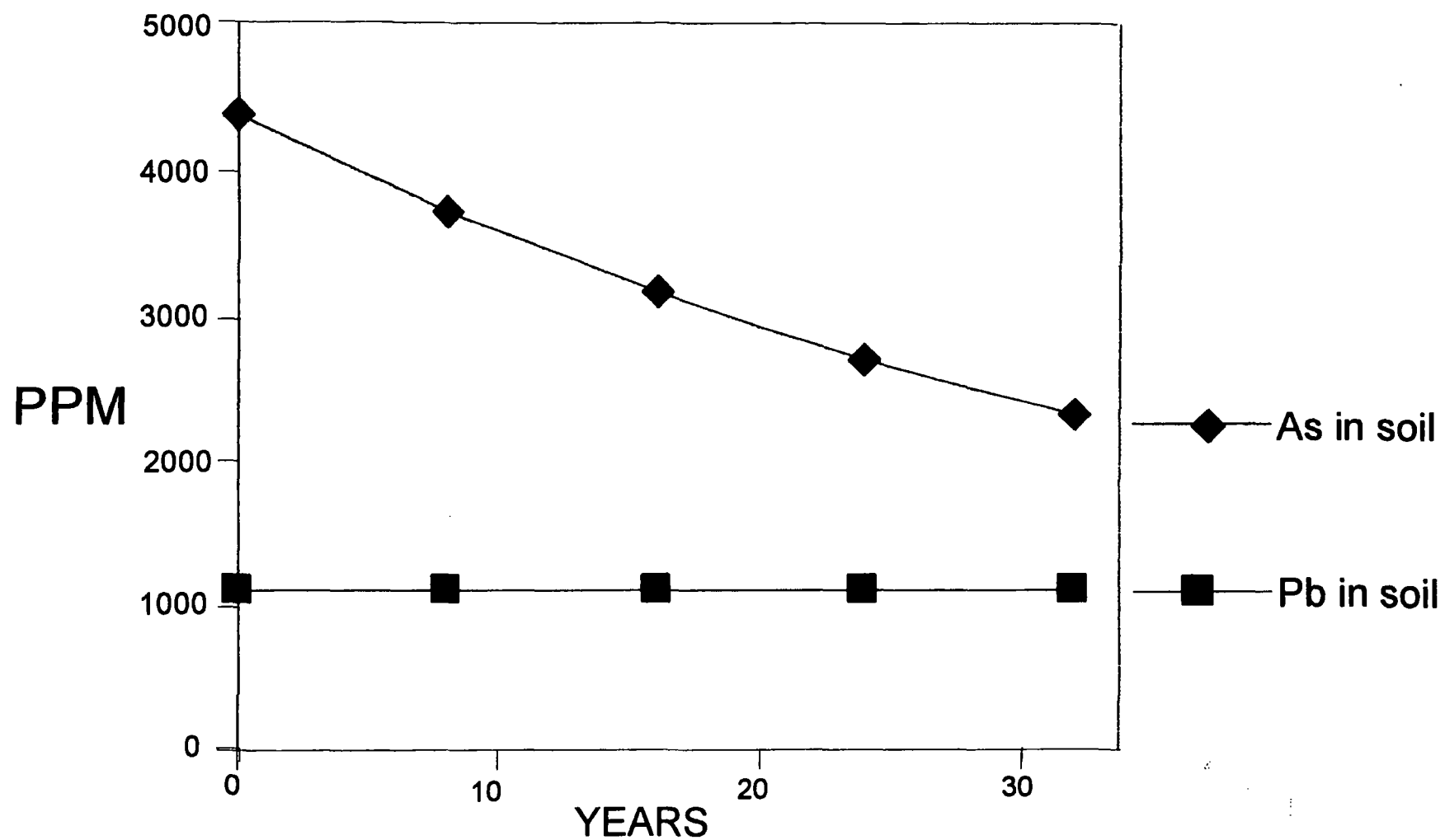


Figure 14. Plot of As and Pb content in a soil versus years of leaching for a synthetic PAX mixture.

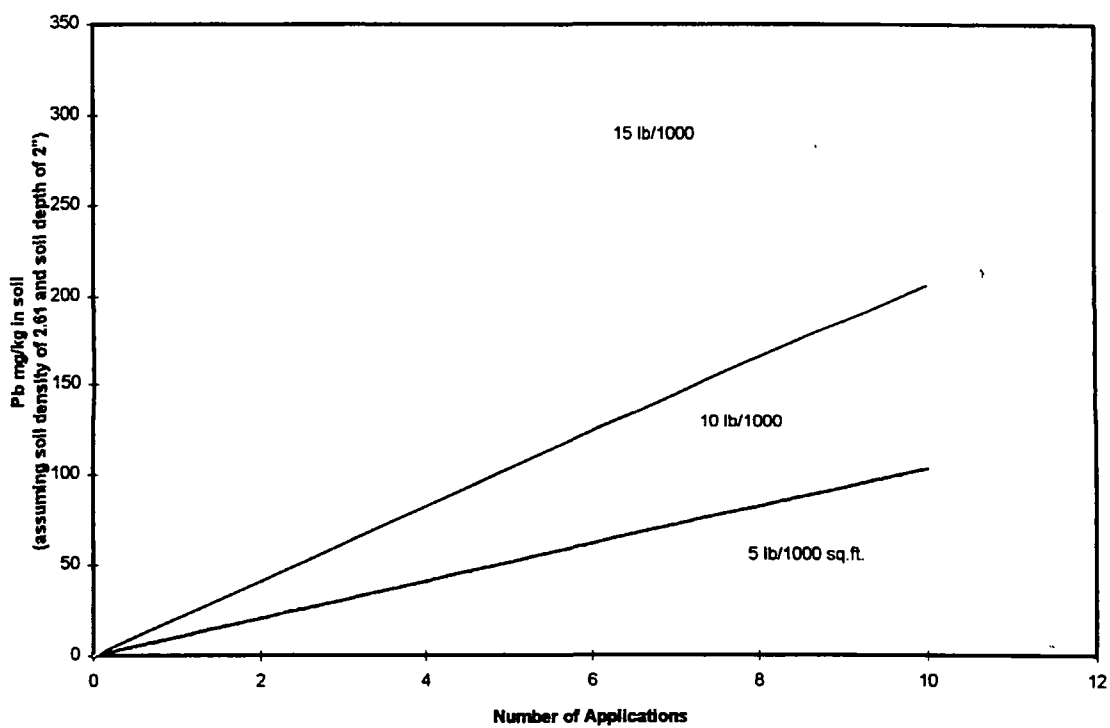
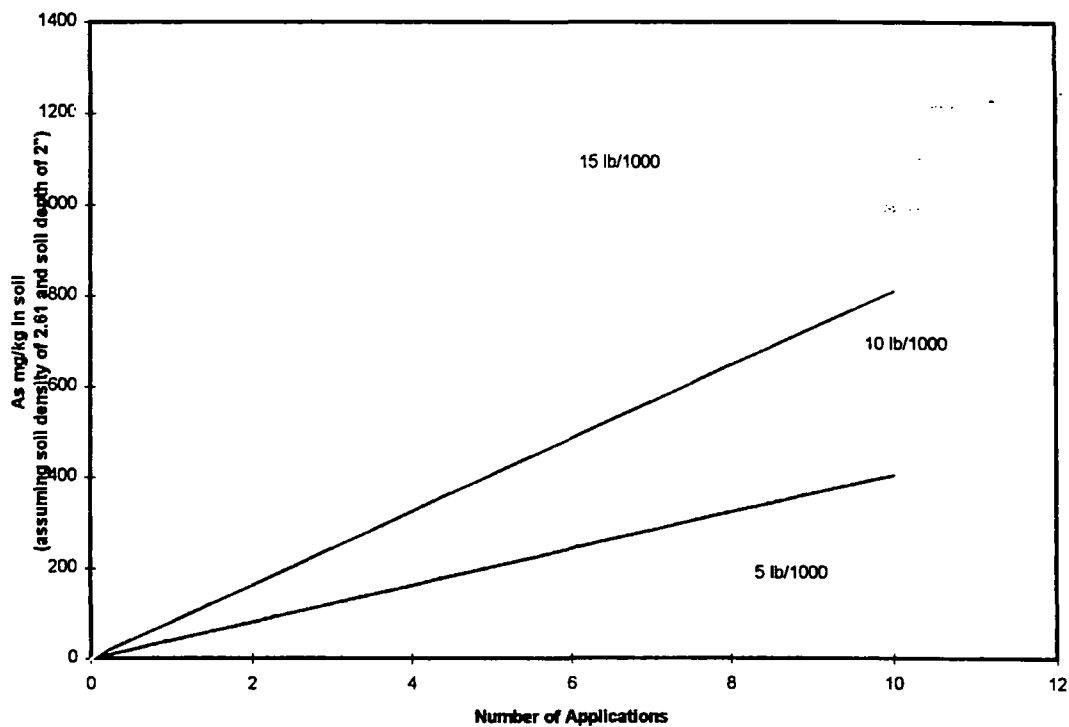
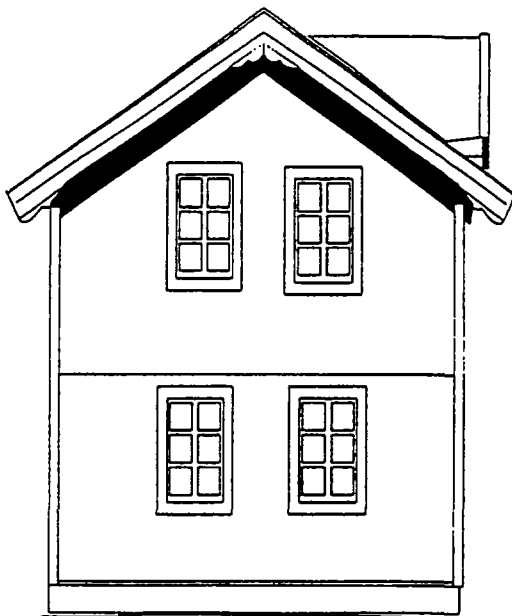


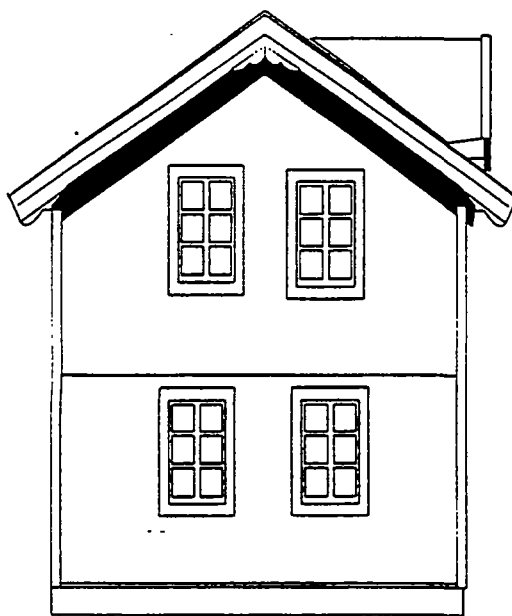
Figure 15. Pb-As concentrations in upper 2" of soils vs number of applications for variable PAX application rates.



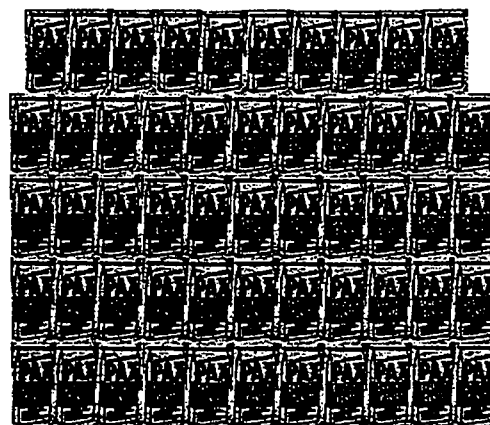
20 lb



Normal heavy application rate (20 lb/1000 square feet = 81 ppm As) dispersed in top 4 inches of soil.



1078 lb



Fifty four times the normal heavy application rate (1078 lb/1000 square feet) would have to have been applied ~32 years ago to have 2333 ppm As remaining in top 4 inches of soil. At 54X the 20lb/1000 square feet application rate there would be 1105 ppm lead in 4 inches of soil after ~30 years (772 ppm Pb is present at 4438 Lincoln).

Figure 16. Normal PAX application compared to application needed to create conditions at 4438 Lincoln.

In addition, the bulk arsenic to lead ratios in the community soils do not always support PAX as a source of the elevated arsenic concentrations. As illustrated in Figure 14, the lead concentration in the PAX-contaminated soil would have to be approximately 1100 mg/kg. The soil at 4438 Lincoln currently has 741 mg/kg lead, far too little especially when one considers the fact that some of the current bulk lead (perhaps 100-300 mg/kg) is likely to have come from paint and/or automobile emissions. For four out of five highly anomalous (>1300 mg/kg arsenic) yards, bulk lead concentrations were too low, relative to arsenic concentrations, to have been from PAX application. Finally, the speciation results are not supportive of PAX as the source to the elevated arsenic concentrations. Approximately one third (11 out of 30) of the community samples contain both As_2O_3 and PbAsO , as would be the case if PAX was applied. When both species are present, arsenic trioxide (the more soluble species) is generally found in greater abundance than would be predicted if PAX were the arsenic source. Approximately 50% (16 out of 30) of all the community samples studied have no PbAsO (the less soluble species) and approximately 25% (7 out of 30) have neither species present.

The assertion by ASARCO that PAX was readily available to the Globeville community may be correct; however, the density of commercial stores selling PAX in the Denver metro area is far greater in other communities, Figure 17, and therefore one would predict that there would be numerous anomalous arsenic sites throughout metro Denver.

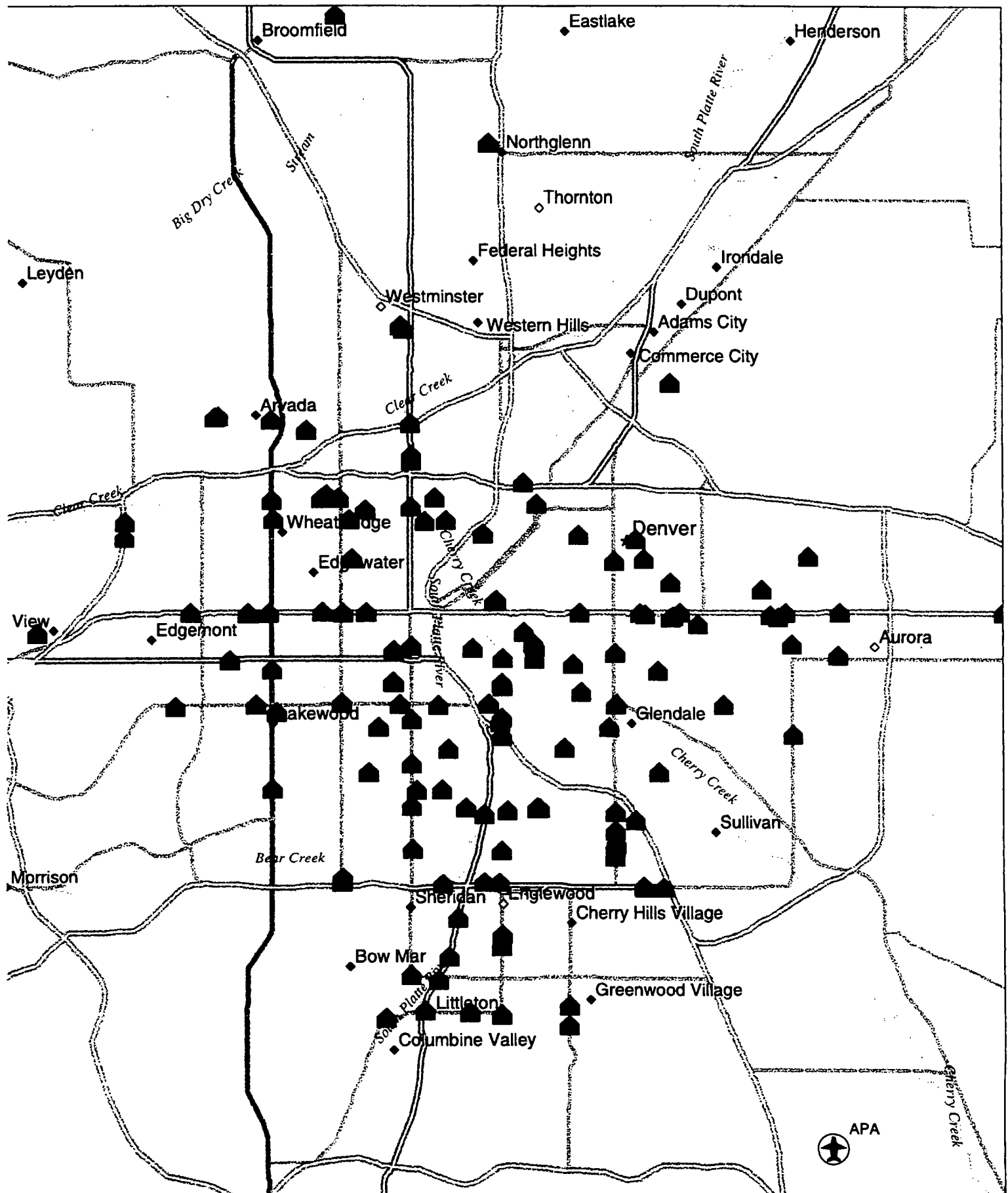


Figure 17. Location of stores selling PAX.

7.0 STACK EMISSIONS

ASARCO contends that the anomalous arsenic concentrations in the Globeville community are not a result of Globe smelter emissions based on the following:

- > the lack of a “snow-drift” distribution of metals distal to the Globe site
- > the clean yard vs dirty yard boundary effect
- > the size and form of arsenic present

Each of these observations has merit; however, elimination of stack emissions as a source may not be the only conclusion one can derive from these and other observations.

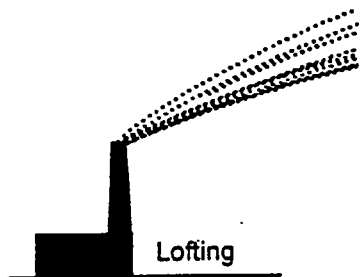
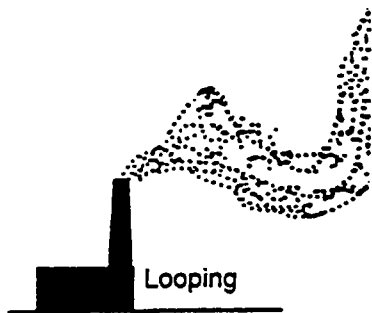
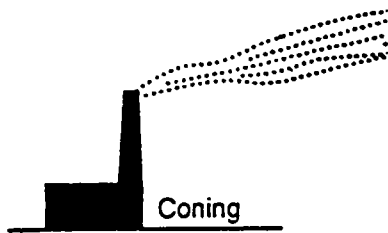
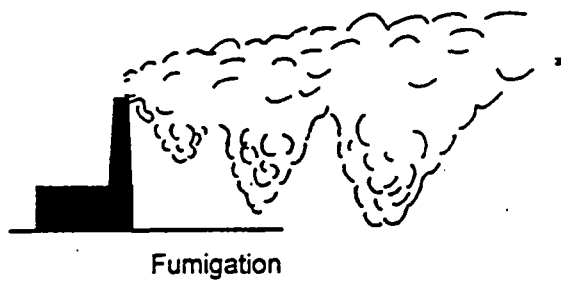
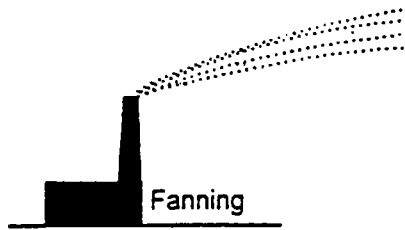
“Snow-drift”

The dispersion of air pollutants is a function of velocity, turbulence, and direction of the wind. Thus dispersion plumes are significantly influenced by predominant wind directions and concentrations within the plume are a function of wind velocity. Turbulence is influenced by meteorological (gusting winds, inversions), structural (stack and building height), and source (emission rates, fumigation events) characteristics. All of these influences can result in plume dispersal patterns that are much different, Figure 18, than the “snow drift” model that ASARCO assumed. Some plume dispersal patterns can deposit very high concentrations of toxic metals in isolated regions downwind from the source. Such an event was documented at Mill Creek,

Montana, where a whole town had to be relocated because it received heavy arsenic loadings during fumigation episodes from a smelter stack some 2500 meters away.

The dilution of stack fumes by these factors is not modeled easily because available algorithms have only been developed for gaseous emissions. Metal fumes sublime based on their vapor pressures, Figure 19, causing plumes to retain certain metals (ie. arsenic, mercury, and antimony) longer than other, lower vapor- pressure metals (lead, copper, and zinc). Elevated concentrations of arsenic are possible without concurrent anomalies of lead or zinc.

Figure 18: Potential plume profiles based on wind stability classes.



Building wake effects

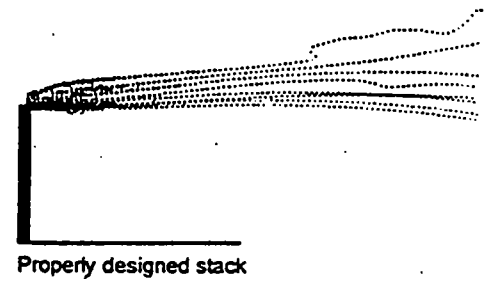
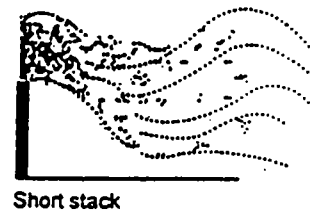
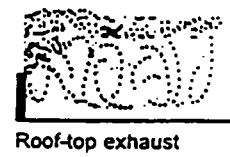
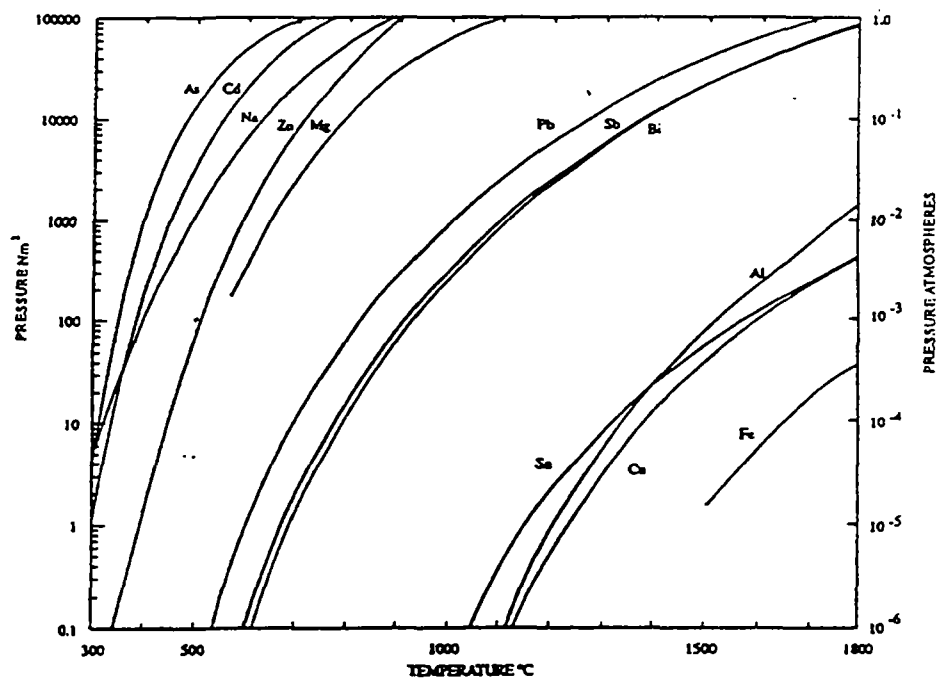


Figure 19. Variation in vapor pressure vs temperature for some pure elements.



Keeping in mind all of the possible influences on plume dispersion, and with the reservation that this author has no special expertise in air modeling, models were run on simulated emissions from the Globe/ASARCO facility in an effort to gain insight into the anomalous arsenic concentrations found approximately 0.8 miles (1300 m) from the facility.

For the above study, site-specific data from the Globe/ASARCO plant were used.

The models (Cooper and Alley, 1986, Lide 1994; and Reynolds et al., 1991) indicate that for stability classes A-C, ground level concentrations are maximized within 400 to 1000 meters of the stack, Figure 21. However, for stability classes D-F, more common to the Globeville area, ground level concentrations can reach maximums of 2000 to 5000+ meters from the source (Figure 20) depending on effective stack height.

Particle-size distribution models indicate, Figure 20, that for particles greater than 100 μm a travel distance of more than 200 meters is unlikely irrespective of stability class. However, particles less than 50 μm in size can effectively reach distances of more than 1000 meters under classes A and B. For the most common stability classes in the Globeville area, particles less than 50 μm in size will have maximum concentrations at distances of 2000 to 5000+ meters, Figure 20.

Overall, the models do indicate that medium, 10-50 μm , particles of arsenic trioxide could have been deposited in the soils south of the Globe/ASARCO facility and depending on stability classes and plume profiles pockets of anomalously high concentrations could be produced.

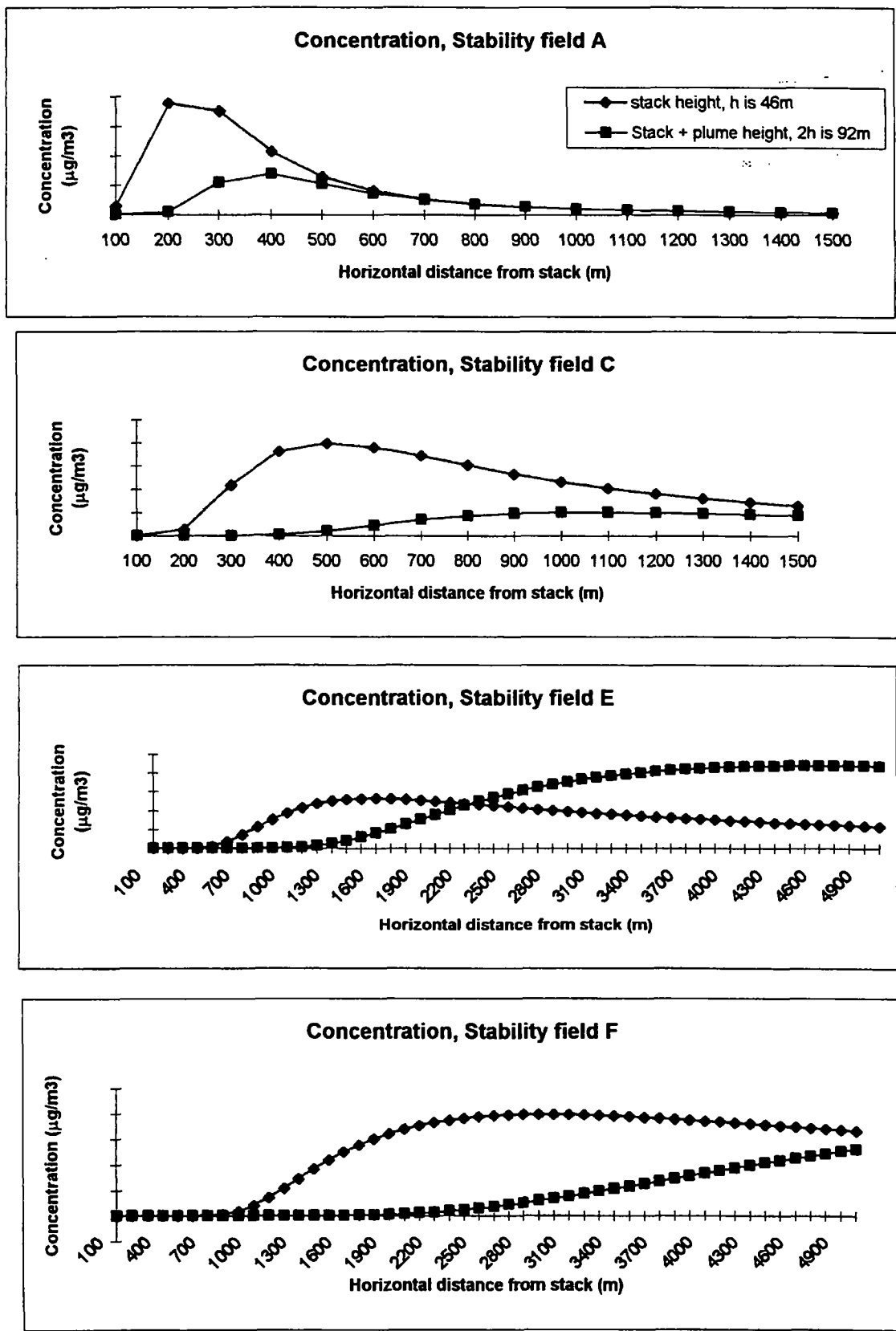


Figure 20. Modeled Arsenic concentrations for variable stability classes and plume heights. Concentrations removed because data source is subject to protective order.

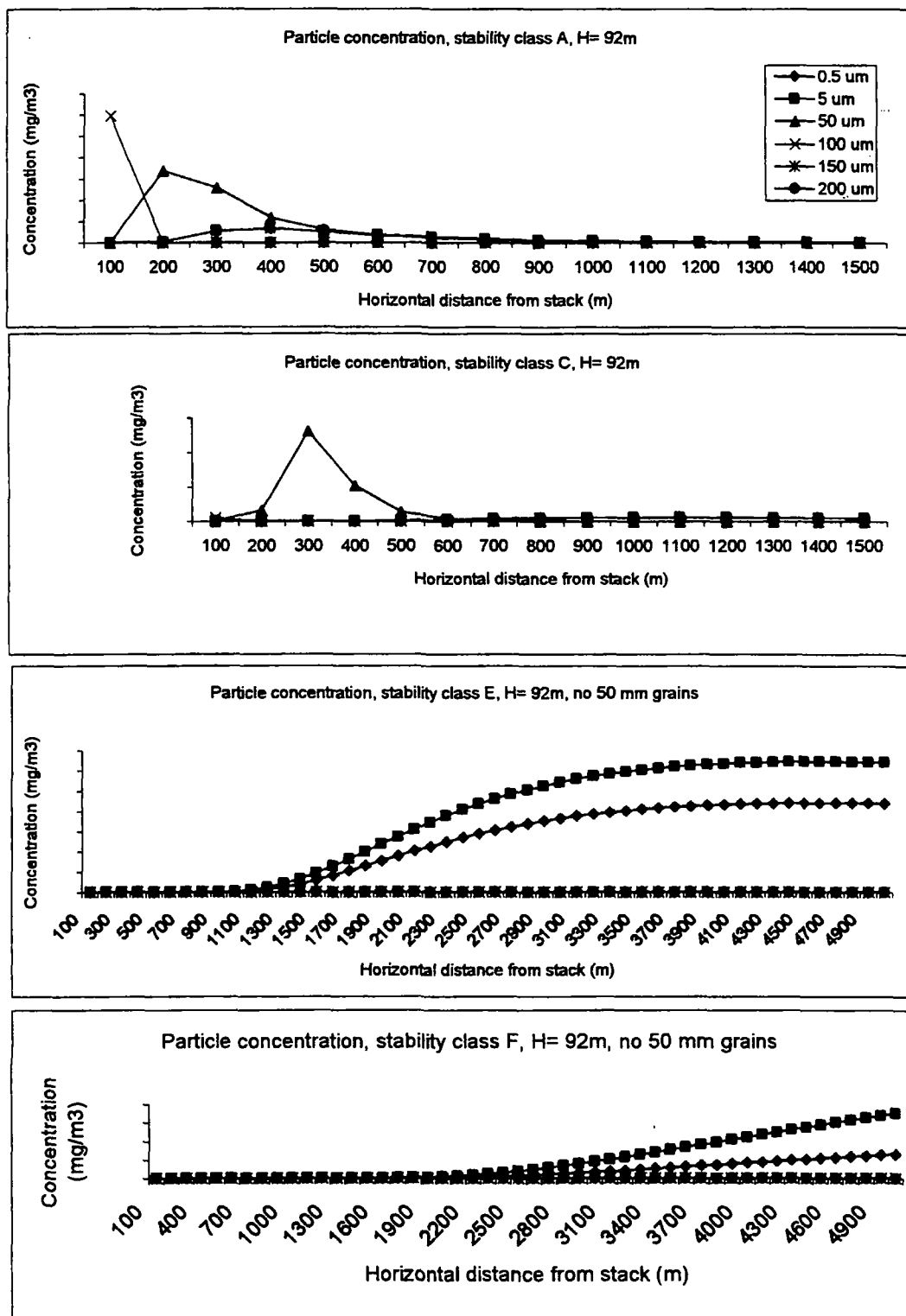


Figure 21. Model Arsenic grain size for variable stability classes and plume heights. Concentrations removed because data source subject to protective order.

In addition, although the “snow drift” or “bulls eye” pattern commonly is found to be associated with stack emissions (Anaconda, Kennecott, and Leadville’s Arkansas Valley), in instances when one has multiple smelters in a growing community for a long period of time (Butte’s Parrot and Colorado, Leadville’s Grant-Union and Leadville) this classical pattern not always is seen. In addition, at Globeville, large areas of non-residential/industrial properties were not sampled, and this may tend to influence kriging patterns.

Yard Boundary

Again, ASARCO’s report contends that the general occurrence of isolated “dirty” yard(s) followed by “clean” yards is indicative of an anthropogenic application of the contaminant. Certainly the random nature and the extent (~2 sq mi) of this pattern would negate a dumping or spill as a possible source; however, this pattern could be the result of yards being “cleaned,” not contaminated. Perhaps the area was uniformly contaminated at some period of time and some property owners brought in clean topsoil or routinely applied fertilizers. These activities would provide a similar areal pattern.

Along with the yard boundary relationship, elevated concentrations of Pb, Zn, and Cd appear to be correlated spatially with arsenic along a 7500 meter, N-S profile (dominant wind direction) through the Globeville community, Figure 22. Therefore, whatever process one envisions for arsenic should also explain the other elevated metals.

Community Soils

N-S Profile

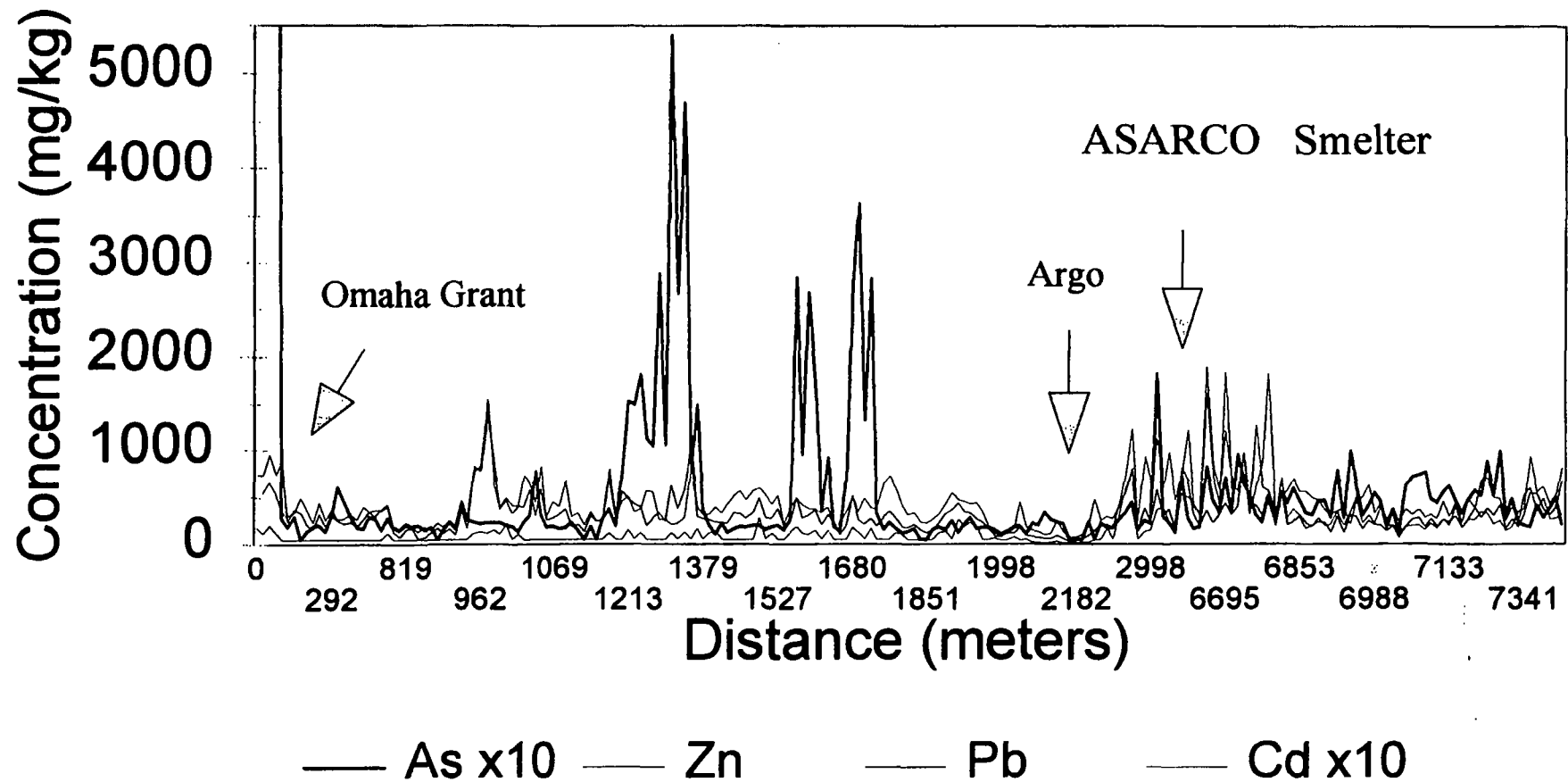
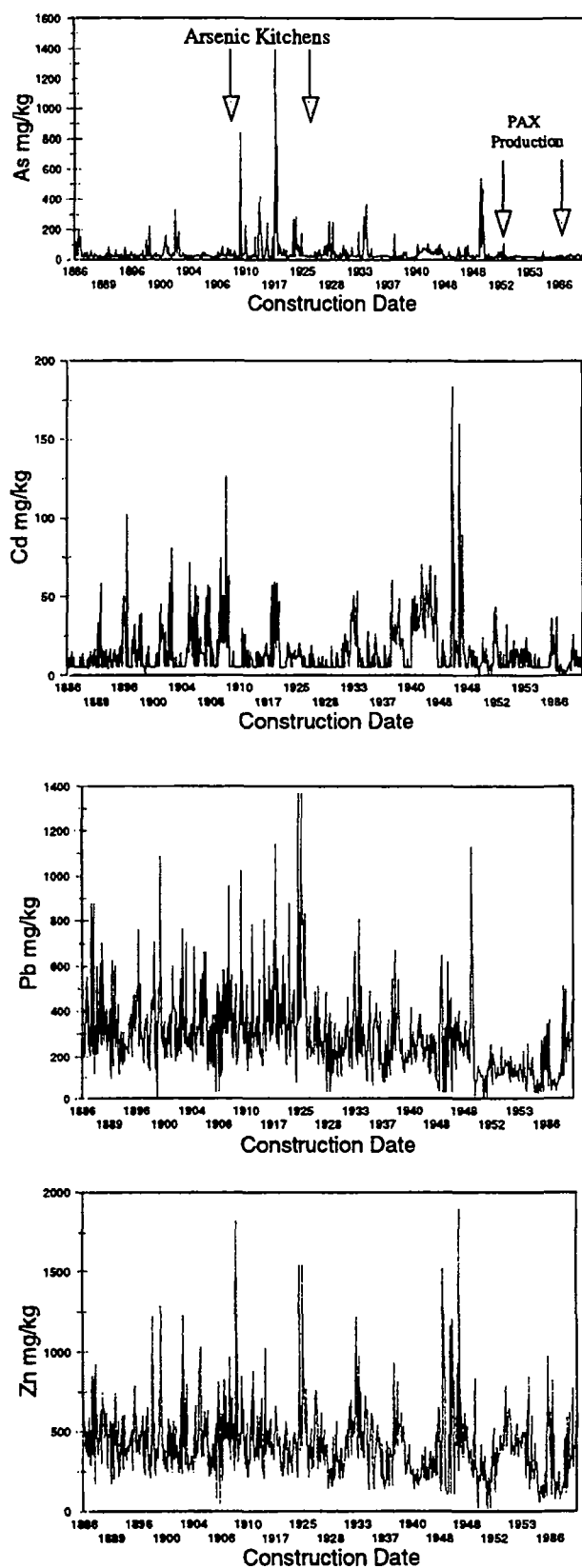


Figure 22. N-S Profile of Community Soil Concentrations

If one examines metal concentration versus home construction date along that same N-S profile through Globeville, Figure 23, two additional observations can be made: 1) elevated concentrations of arsenic are not found in yards younger than 1950, although the other metals continue to be found above background, and 2) the highest frequency of elevated arsenic values are found in yards that have construction dates centered on the window when the arsenic kitchens were in full production. Neither of these observations offer a definitive answer to the source of the arsenic anomaly, but would tend not to support PAX as the source.

FIGURE 23. Globville N-S Profile: Metal Concentration vs Property Construction Date.



8.0 APPORTIONMENT

Based on the results from the arsenic speciation study an attempt to apportion the total soil arsenic to most probable sources was made using the Min_{As} values (Table 5). Three specific categories for the apportionment were made: pyrometallurgical arsenic, non-specific soil-forming arsenic, and As_2O_3 . Criteria for each of these categories were as follows:

Pyrometallurgical Arsenic: PbAsO , CaAsO , AlAsO , SbAsO , FeAsO , PbMO , AsMO

Soil-Forming Arsenic: Fe oxide, Mn oxide, phosphate, and clays

Arsenic Trioxide: As_2O_3

Pyrometallurgical species were chosen based on data from site-specific, ASARCO plant (this study; EnviroGroup, 1997) samples, metallurgical literature (Fergusson, 1990), and previous studies (Drexler, 1995,1997; Thorton 1995). The As_2O_3 category contains only the species As_2O_3 ; however, a portion (4.4% Rm_{As}) of this category has been assigned to a pyrometallurgical source, based on the average occurrence found on the ASARCO plant site (Figure 2). The soil-forming arsenic phases are most likely the result of solubilized arsenic, released from the other two populations that are now sequestered (by sorption) in common, soil-forming mineral phases. Since at least some of the bulk arsenic found in this category may have come from pyrometallurgical processes, a percentage of the “non-source specific” category (based on the

percentage of pyrometallurgical arsenic identified in each sample) has been assigned to this source. Results of the apportionment are summarized in Table 7. The apportionment calculation indicates that even if As_2O_3 cannot be directly associated with a pyrometallurgical source, 54% of the residential yards with bulk arsenic greater than 70 mg/kg (the site action level) would have had pyrometallurgical arsenic greater than 28 mg/kg. In addition, 92% of the yards with anomalously high (>300 mg/kg) bulk arsenic levels would have had pyrometallurgical arsenic above the 28 mg/kg voluntary remediation level.

Table 7. Globeville Residential Soils: Apportionment Calculations.

Sample		4363 Lincoln-R	4992 Lincoln
As (ppm)		81	3873
Pyrometallurgical			394.0
Non-Source Specific		81.0	42.0
(using %Pyrometallurgical)	Non-Source Specific-Pyrometallurgical		4.3
	Non-Source Specific ?	81.0	37.7
Arsenic Trioxide			3438.0
(using 4.4% from plant)	Arsenic Trioxide-Pyrometallurgical		151.3
	Arsenic Trioxide-?		3286.7
Total Pyrometallurgical Arsenic			394.0

Table 7. Globeville Residential Soils: Apportionment Calculations.

Sample	4600 Grant	609619	609627	609628	609629	609630	609631	GV-5
As (ppm)	13	862	20	1524	720	524	516	47
Pyrometallurgical	12.8	128.7		219.1	183.0	77.7	70.2	1.9
Non-Source Specific	0.2	51.3	20.0	72.5	33.3	212.6	50.1	5.6
(using %Pyrometallurgical)	0.2	7.7		10.4	8.5	31.3	6.8	0.2
	0.0	43.6	20.0	62.1	24.8	180.9	43.3	5.4
Arsenic Trioxide		682.0		1232.3	503.7	233.6	395.5	39.0
(using 4.4% from plant)		30.0		54.1	22.2	10.3	17.3	1.7
		652.0		1178.1	481.5	223.5	378.0	37.3

Table 7. Globeville Residential Soils: Apportionment Calculations.

Table 7. Globeville Residential Soils: Apportionment Calculations.

Sample	SO-1	SO-7	SO-10	SO-13	SO-14	SO-22	4422 Delaware-F
As (ppm)	107	93	118	63	75	55	136
Pyrometallurgical	80.4		4.2	20.0	10.6	8.8	75.6
Non-Source Specific	26.6	29.9	4.8	42.9	20.5		60.4
(using %Pyrometallurgical)	20.0		0.2	13.6	2.9		33.6
	6.6	29.9	4.7	29.3	17.6		26.8
Arsenic Trioxide		63.1	108.9		43.7	46.2	
(using 4.4% from plant)		2.8	4.8		1.9	2.0	
		60.3	104.1		41.8	44.1	

Table 7. Globeville Residential Soils: Apportionment Calculations.

Sample	4425 Pennsylvania-F	4428 Lincoln-F	4438 Lincoln-F	4460 Pennsylvania-F
As (ppm)	43	459	2200	200
Pyrometallurgical	2.5	35.3	171.8	18.8
Non-Source Specific	40.4	54.1	13.8	2.2
(using %Pyrometallurgical)	2.3	4.2	1.1	0.2
	38.1	49.9	12.7	2.0
Arsenic Trioxide		369.6	2014.5	178.9
(using 4.4% from plant)		16.3	88.6	7.9
		353.3	1925.8	171.1

Table 7. Globeville Residential Soils: Apportionment Calculations.

Sample	4460 Pennsylvania-R	610606	609608	609620	GV-4	SO-15	SO-16
As (ppm)	441	800	402	1348	779	1800	30
Pyrometallurgical	15.1	474.2	298.7	47.5	64.1	194.1	10.5
Non-Source Specific	27.7	49.7	103.3	33.6	52.4	46.0	19.5
(using %Pyrometallurgical)	0.9	29.5	76.7	1.2	4.3	5.0	6.8
	26.7	20.2	26.5	32.4	48.1	41.0	12.6
Arsenic Trioxide	398.2	275.1		1266.9	662.6	1559.9	
(using 4.4% from plant)	17.5	12.1		55.7	29.2	68.6	
	380.7	263.0		1211.2	633.4	1491.2	

Table 7. Globeville Residential Soils: Apportionment Calculations.

Table 7. Globeville Residential Soils: Apportionment Calculations.

Sample	SO-10	770	9190	9232	9742	9779	71
As (ppm)	118	181	116	103	168	146	170
Pyrometallurgical		106.0	33.9	77.6			10.6
Non-Source Specific	18.7	75.0	82.1	25.4	167.7	145.9	32.2
(using %Pyrometallurgical)		43.9	24.0	19.2			2.0
	18.7	31.1	58.1	6.3	167.7	145.9	30.2
Arsenic Trioxide	99.3						127.2
(using 4.4% from plant)	4.4						5.6
	94.9						121.6

9.0 FURTHER STUDIES

The conclusions reached in this report are based on review of available data, which was primarily collected to protect the public health and not to determine the specific source(s) of a particular metal. Therefore, additional data should be collected that could aid in the final identification of the source(s) of arsenic within the Globeville area soils. These data include:

Detailed examination of yards that contain the highest arsenic concentrations including; micro-XRF over 0-18." Samples should be collected from areas not currently sampled such as commercial sites, alleys, railroad rights-of-way, farmland, I-70 rights-of-way, and along the Platte River terrace.

Samples should be collected from the NW corner of the Globe plant, below 6-inch depth, where one finds elevated arsenic concentrations with low Cd, Pb and Zn.

Column studies should be run using soil profiles that more characteristically represent the Globeville community.

More samples should be collected in the communities of Swansea/Elyria, and west of I-25.

Other "fingerprint" elements should be investigated (i.e., Ca, Mg, and Sb).

A sampling program should be conducted in another similar neighborhood distant from the plant, to determine if high levels of arsenic are present.

10.0 CONCLUSIONS

Based on the data presented in this report the following conclusions can be reached with respect to the occurrences of arsenic found in residential soils from the Globeville area.

- ▶ Arsenic trioxide is the dominant contaminant in the anomalous soils.
- ▶ The strong correlation between As_2O_3 and AsSbO is indicative of a pyrometallurgical source.
- ▶ No correlation exists between As_2O_3 and PbAsO ; a correlation would be expected if the arsenic source were PAX.
- ▶ For properties with highly anomalous (>1300 mg/kg) bulk arsenic concentrations, arsenic concentrations are often high relative to bulk lead and are not found in the proportions expected in PAX.
- ▶ For properties with moderate arsenic concentrations, metal species are not found in the proportions expected in PAX.
- ▶ Yards have phases indicative of a pyrometallurgical source (In , Se , Tl , CaAsO , AsMO Slag, FeAsO , and PbAsO).
- ▶ 68% of yards speciated with bulk arsenic >28 mg/kg have pyrometallurgically apportioned arsenic >28 mg/kg.

The available data does not provide a clear indication as to how the arsenic trioxide was deposited onto individual yards. However, based on the data reviewed in this report it is my opinion that the arsenic in the Globeville area is the result of both smelter-stack emissions and of a commercial-grade of arsenic trioxide that is not likely to have been deposited by normal stack fallout.

11.0 REFERENCES

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PHOTO 1. EMPA backscatter photomicrographs and EDS x-ray spectra.

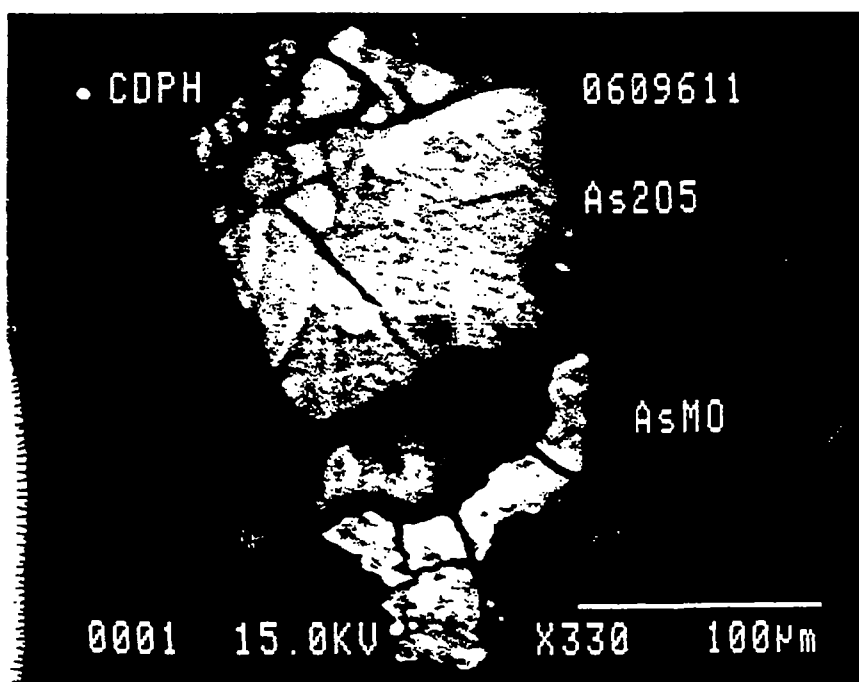
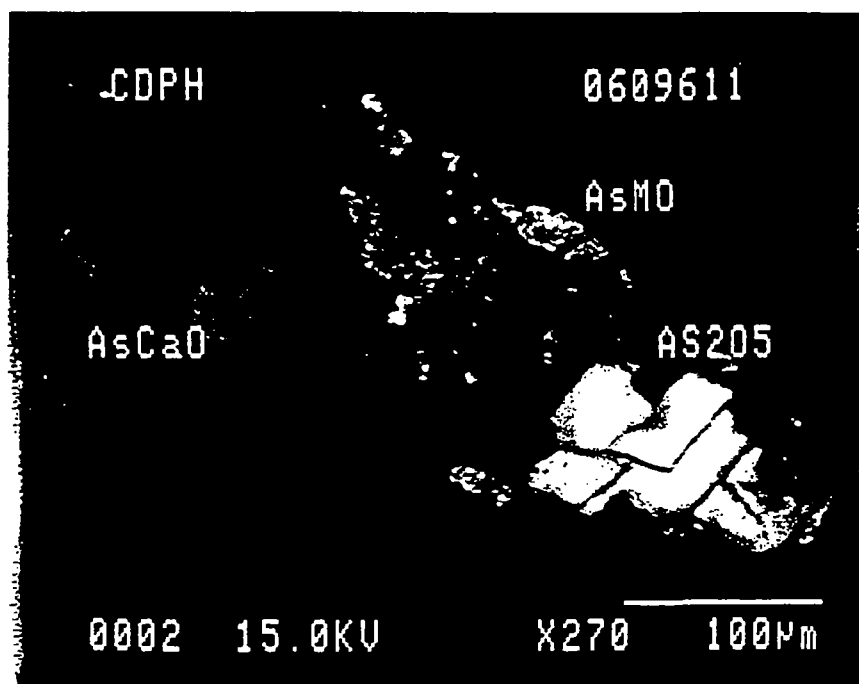


PHOTO 2. EMPA backscatter photomicrographs and EDS x-ray spectra.

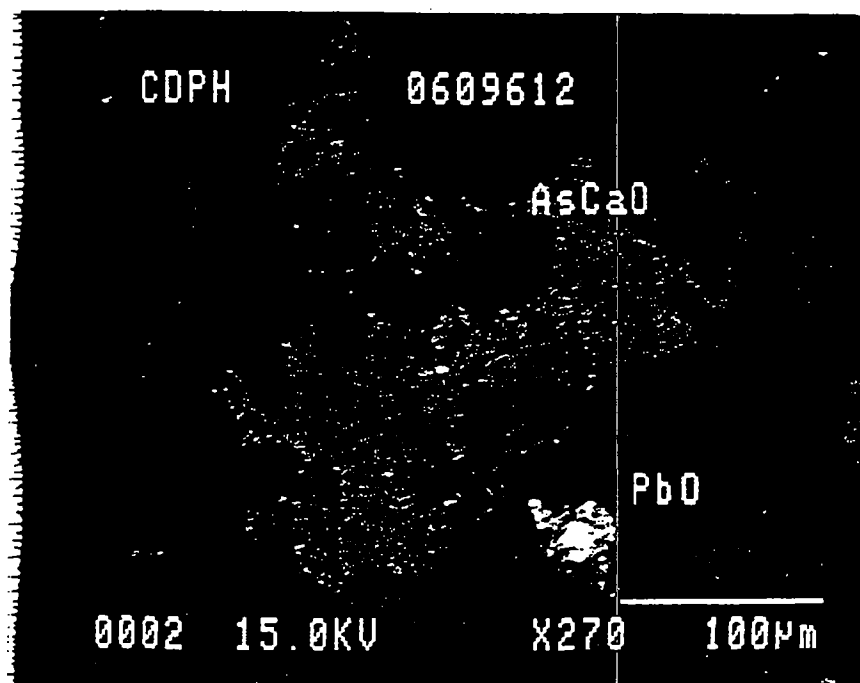


PHOTO 3. EMPA backscatter photomicrographs and EDS x-ray spectra.

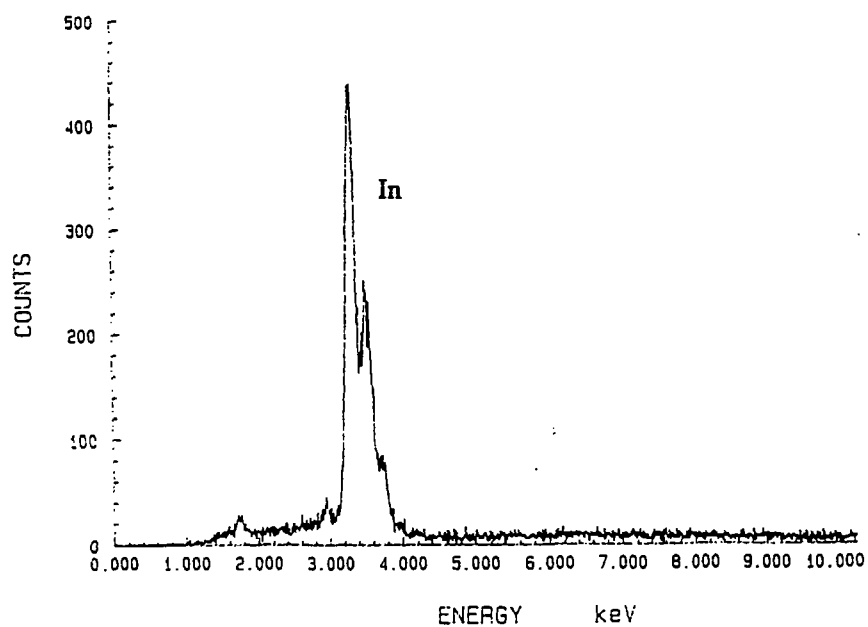
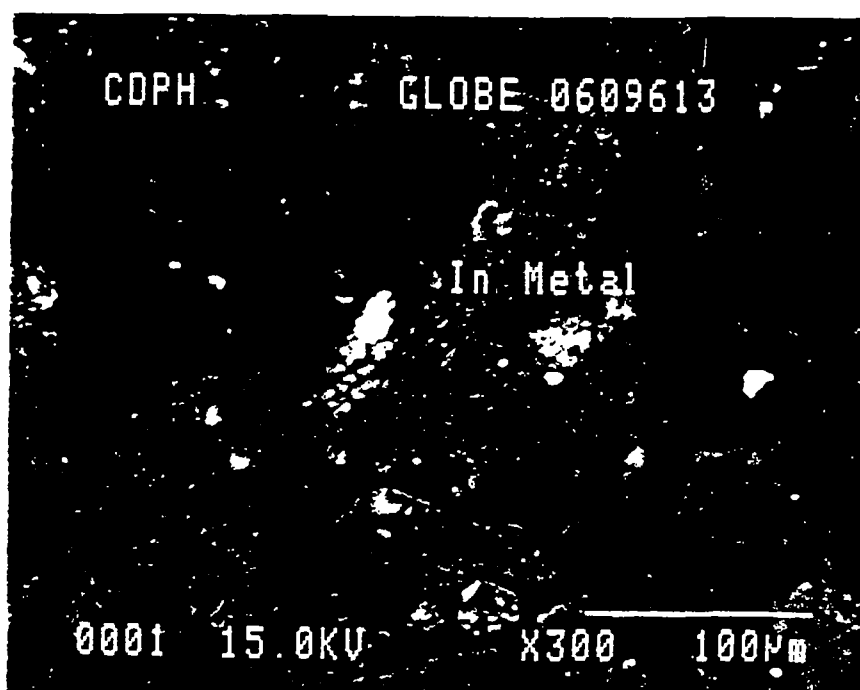


PHOTO 4. EMPA backscatter photomicrographs and EDS x-ray spectra.

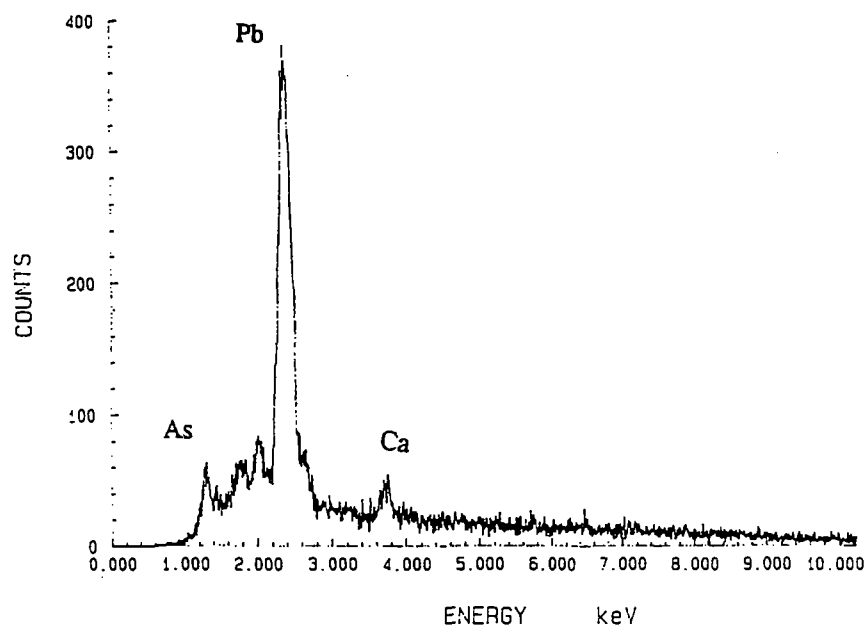
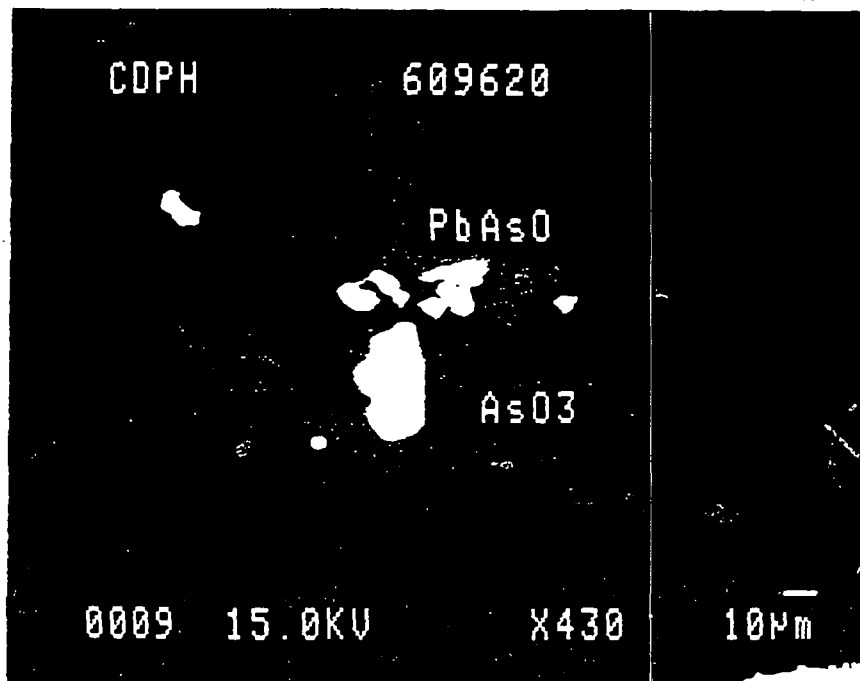


PHOTO 5. EMPA backscatter photomicrographs and EDS x-ray spectra.

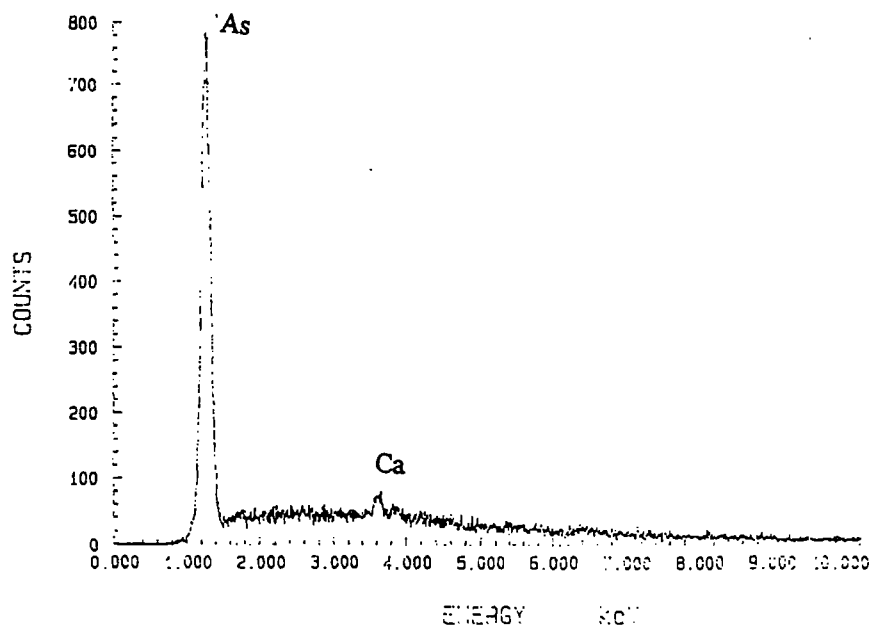
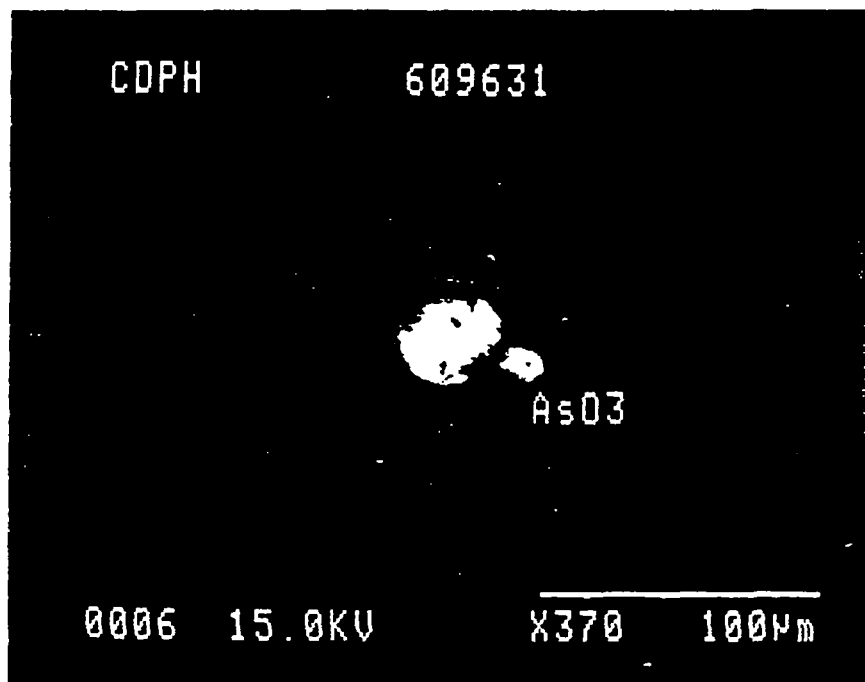


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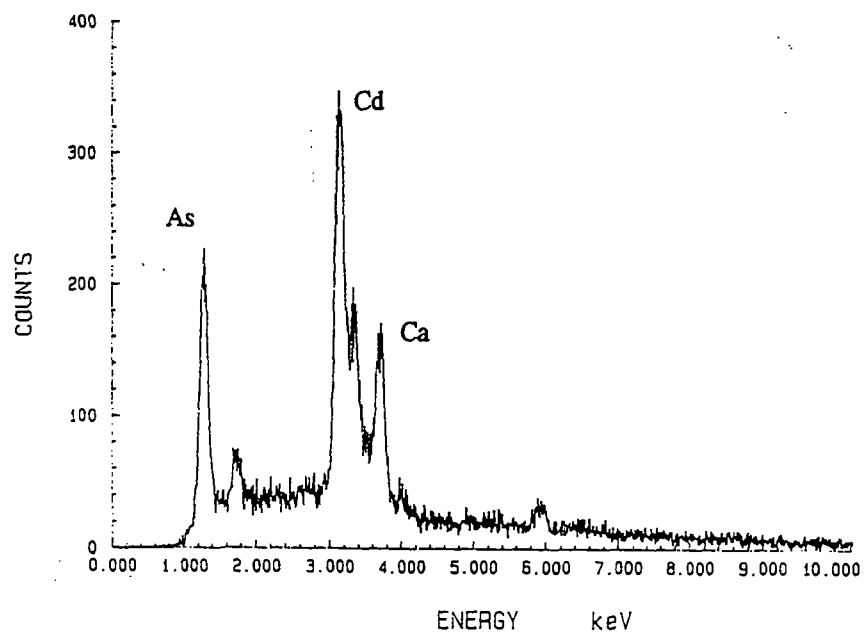
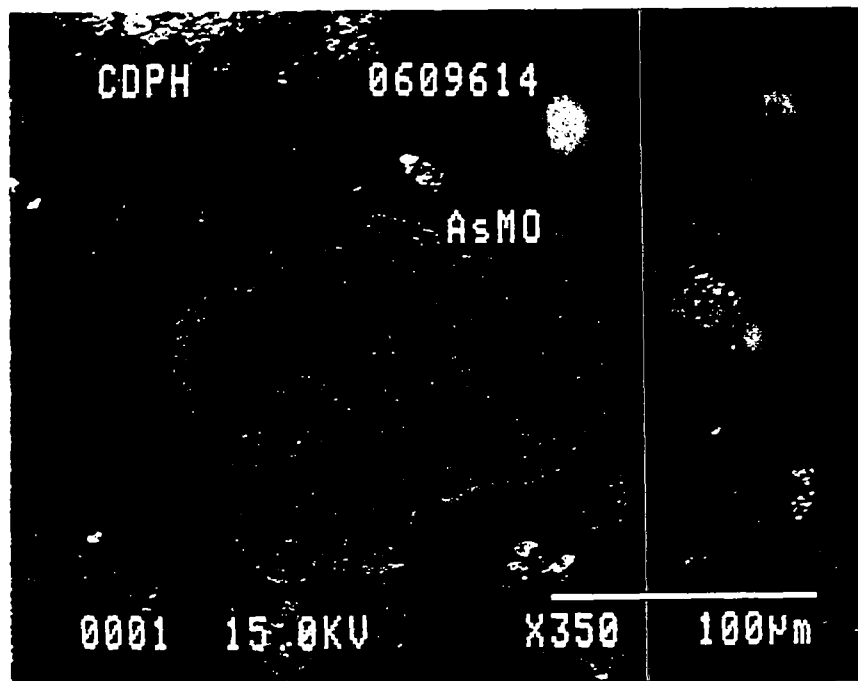


PHOTO 7. EMPA backscatter photomicrographs and EDS x-ray spectra.

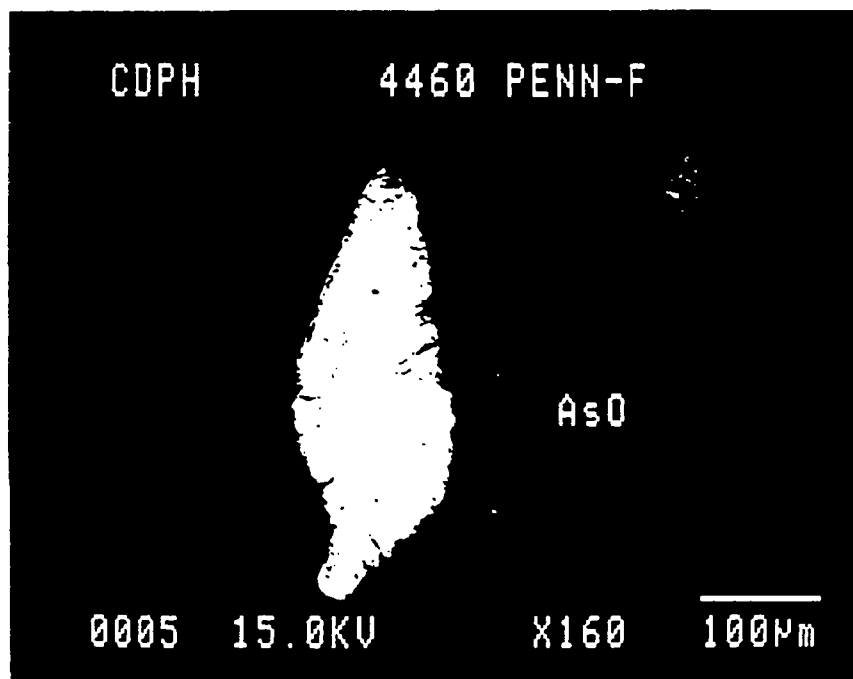
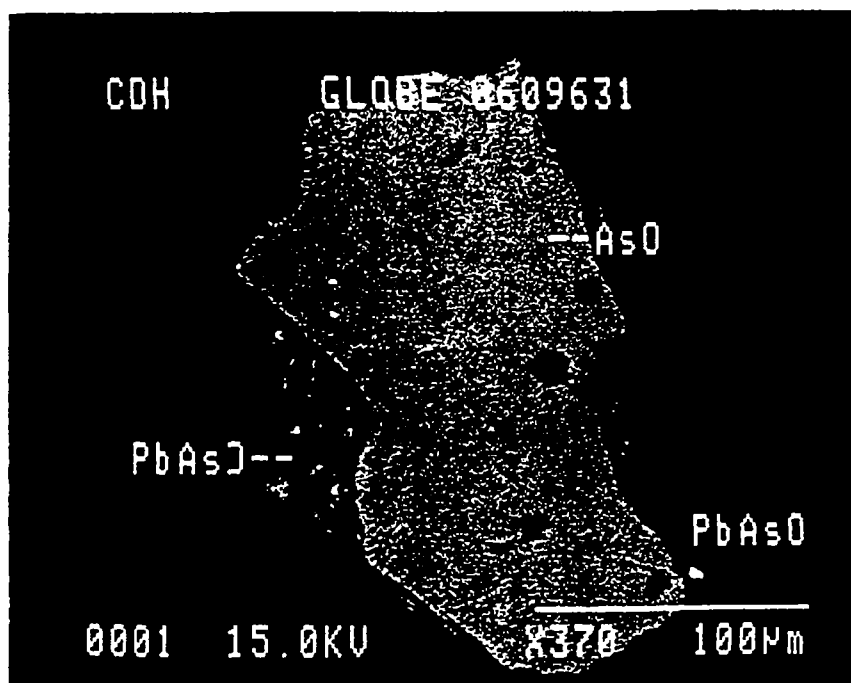


PHOTO 8. EMPA backscatter photomicrographs and EDS x-ray spectra.

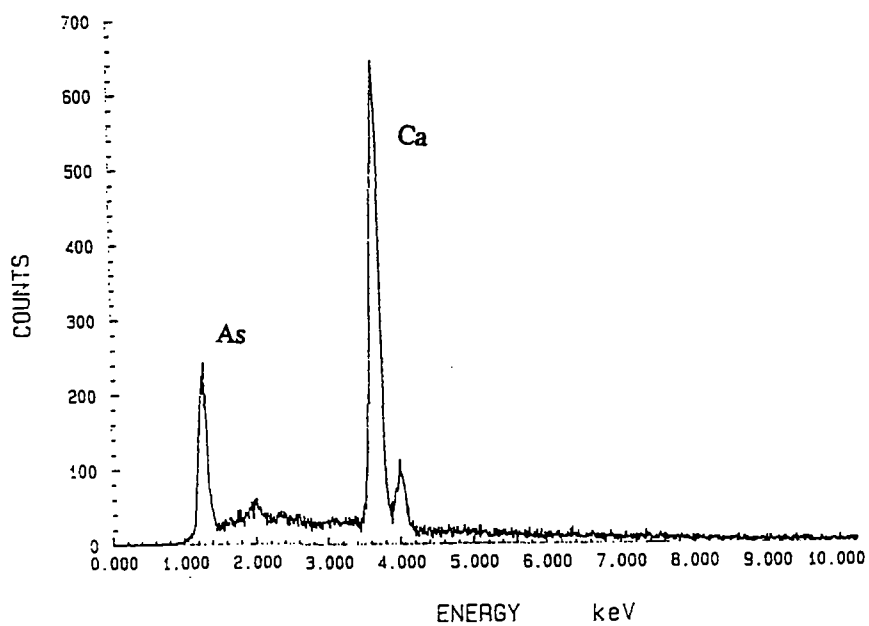
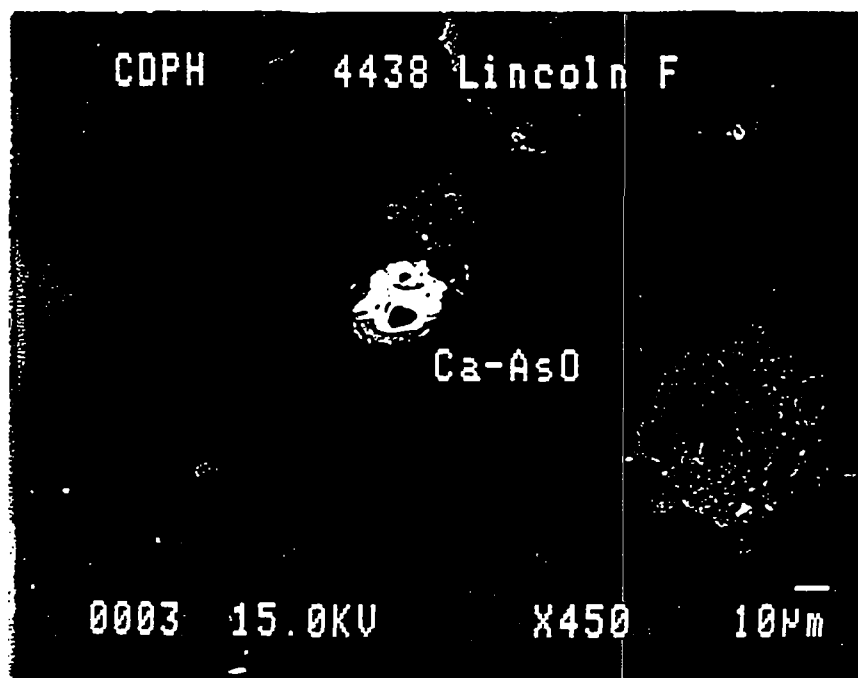


PHOTO 9. EMPA backscatter photomicrographs and EDS x-ray spectra.

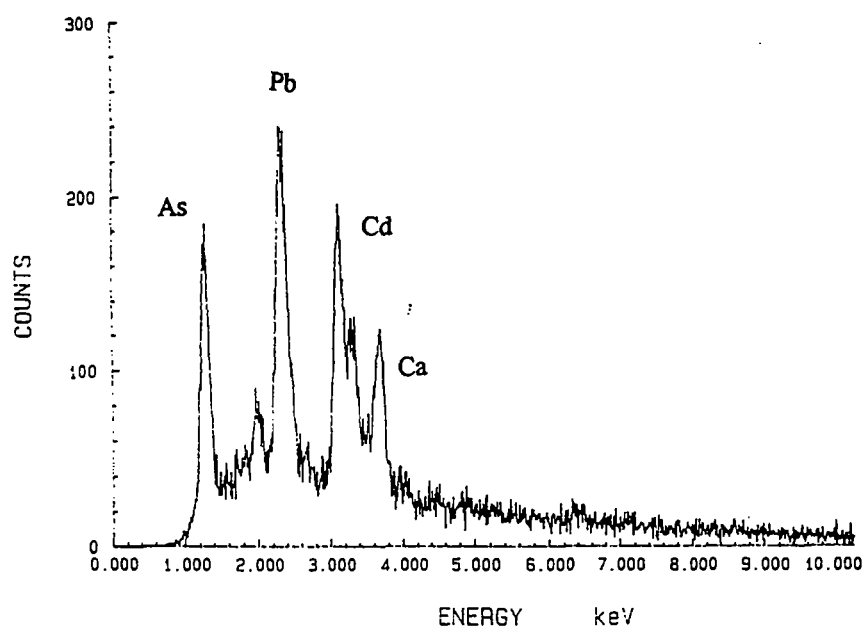
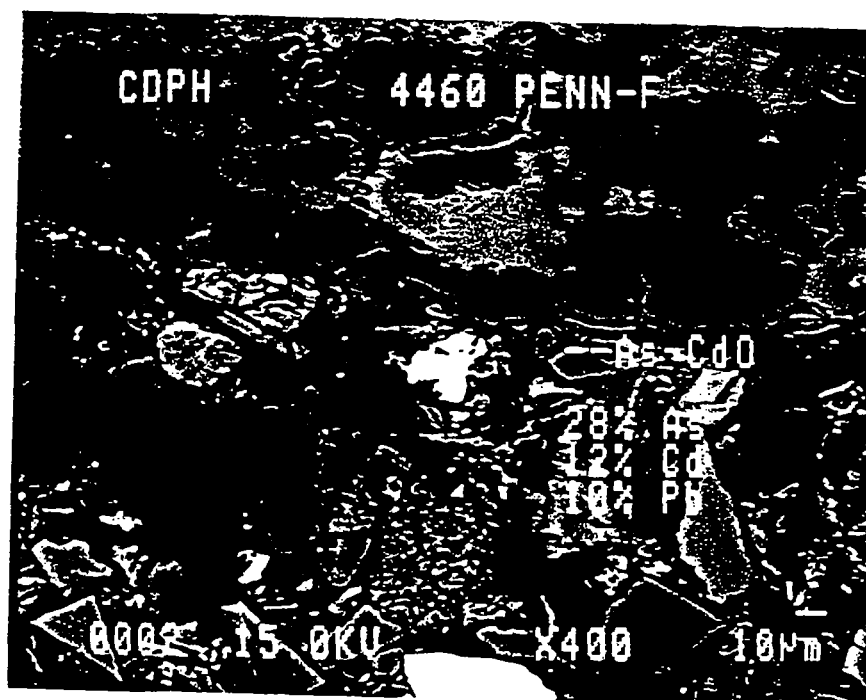


PHOTO 10 EMPA backscatter photomicrographs and EDS x-ray spectra.

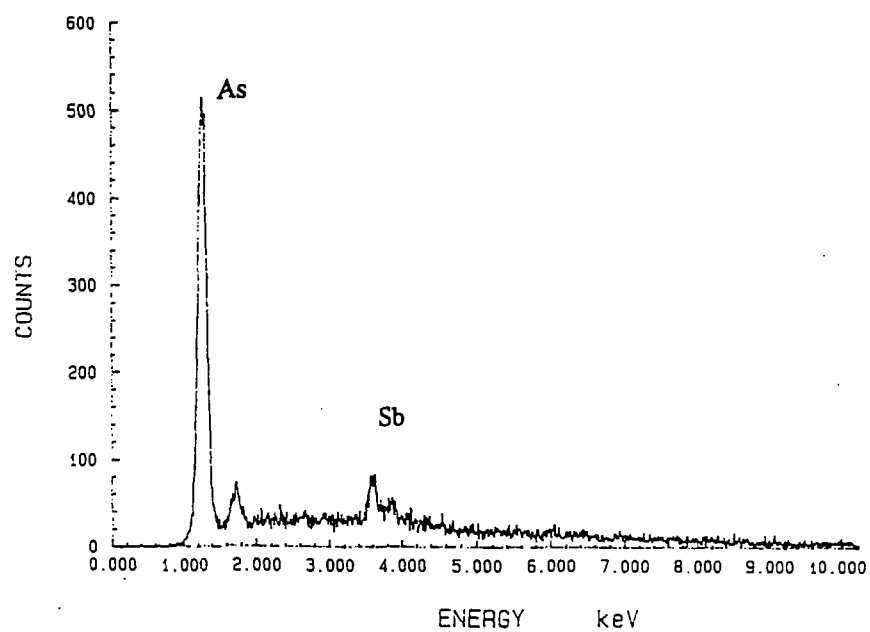
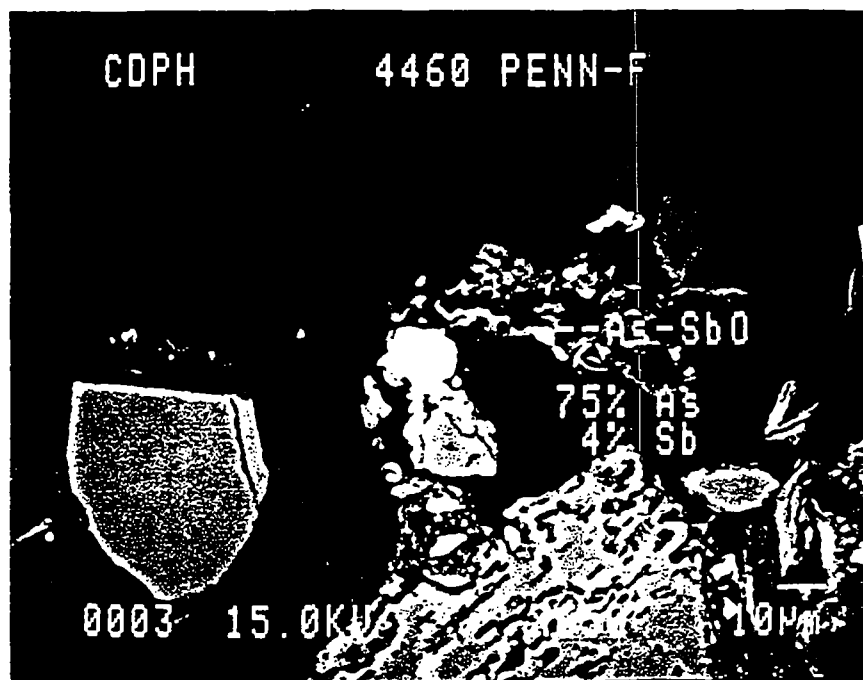


PHOTO 11. EMPA backscatter photomicrographs and EDS x-ray spectra.

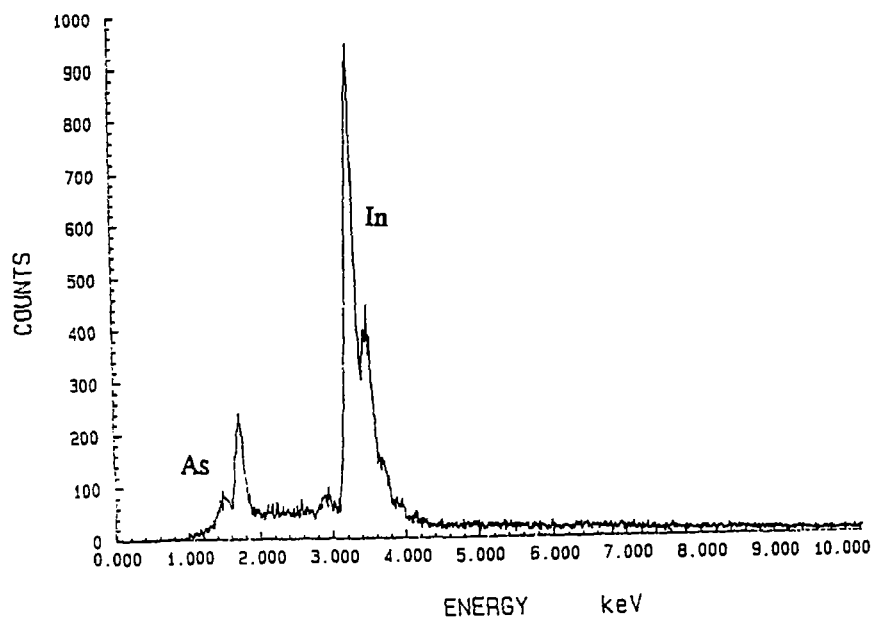
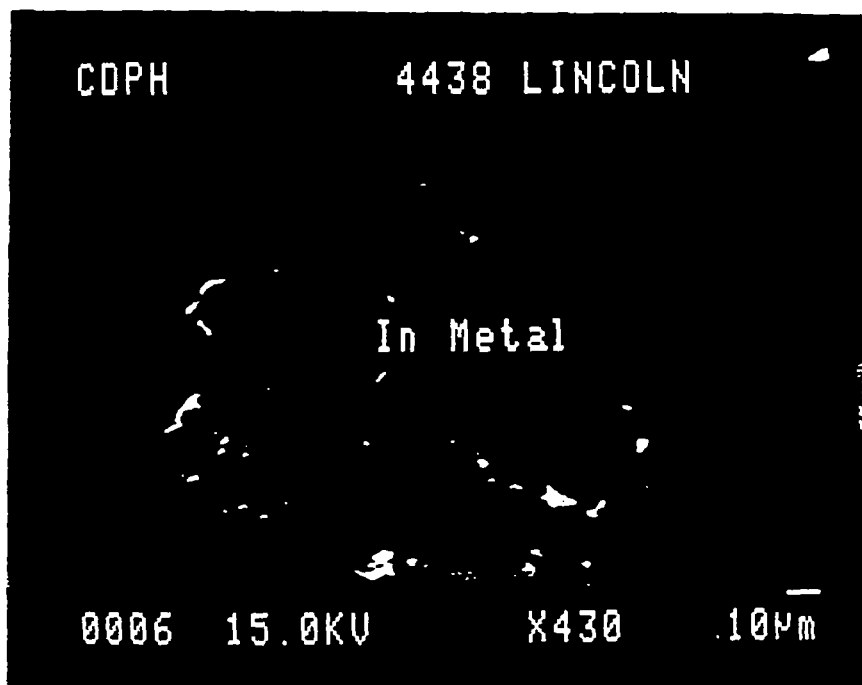




PHOTO 12. EMPA backscatter photomicrographs and EDS x-ray spectra.

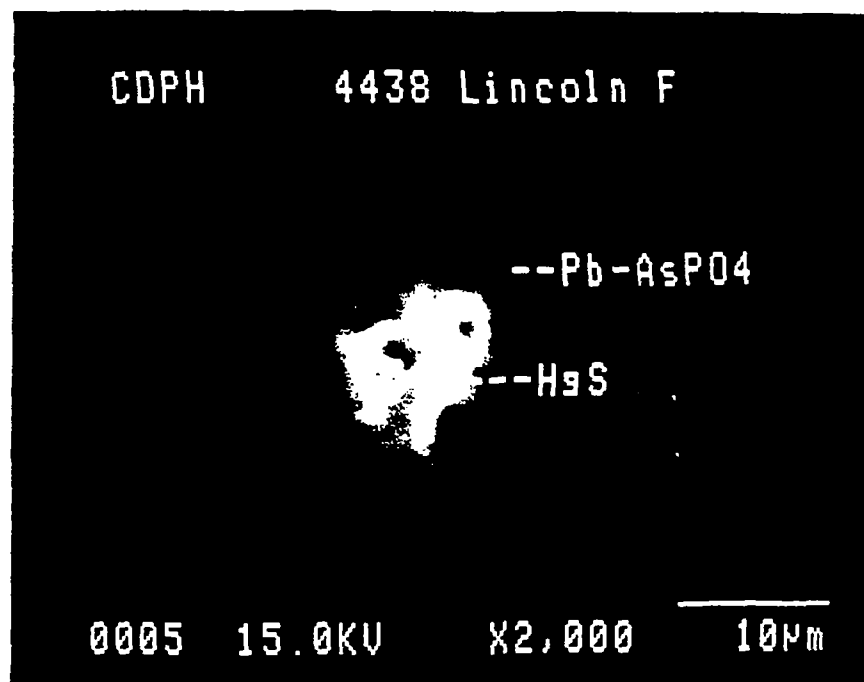


PHOTO 13. EMPA backscatter photomicrographs and EDS x-ray spectra.

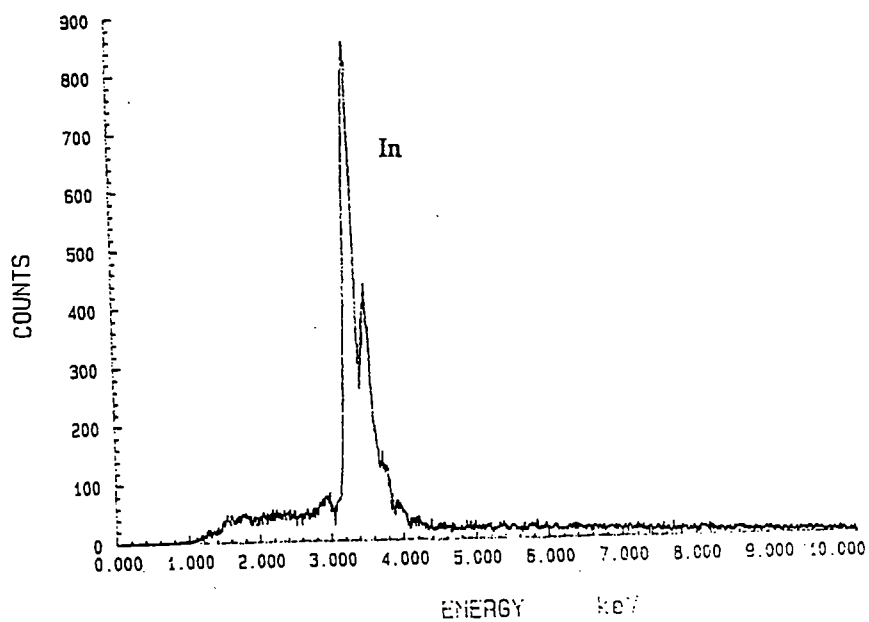
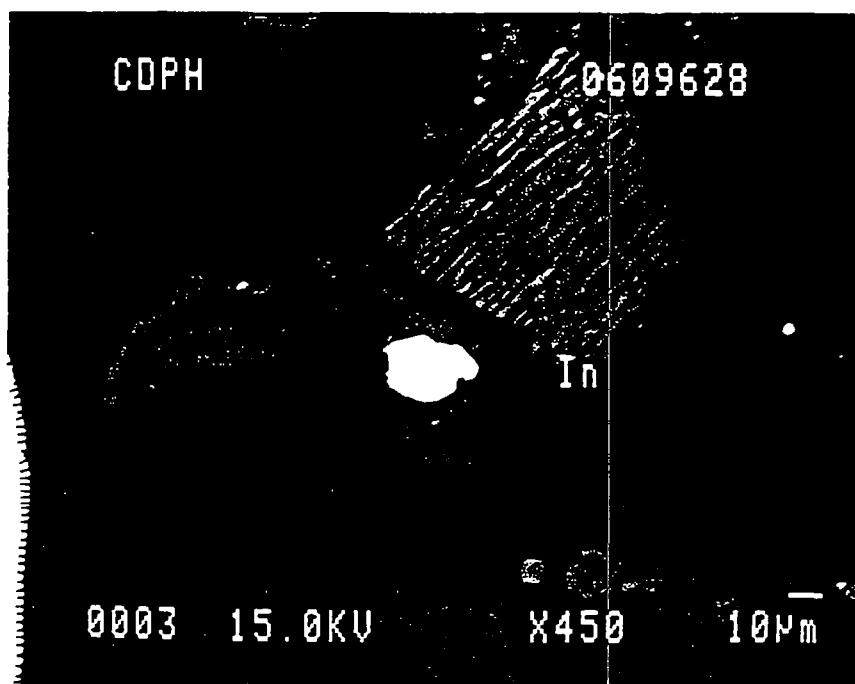


PHOTO 14. EMPA backscatter photomicrographs and EDS x-ray spectra.

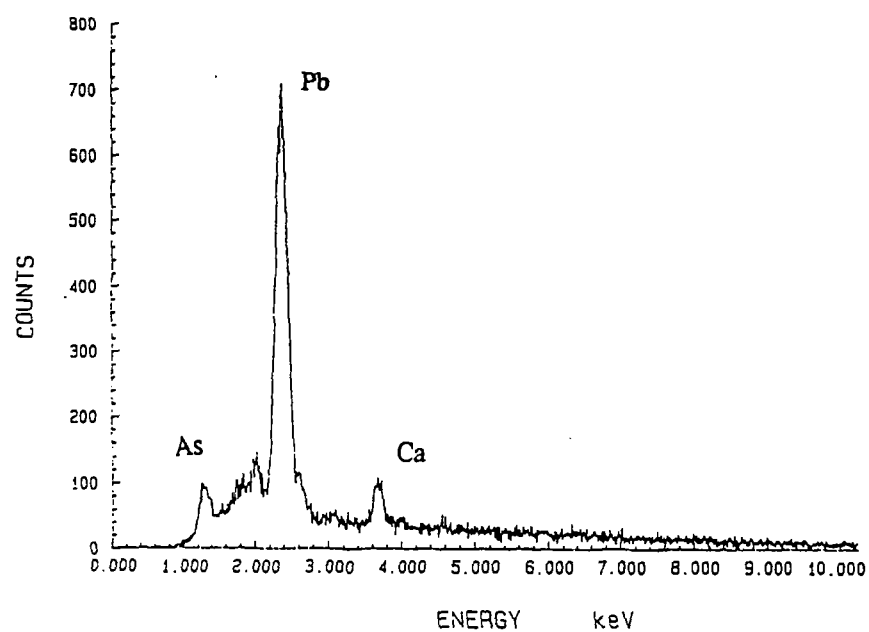
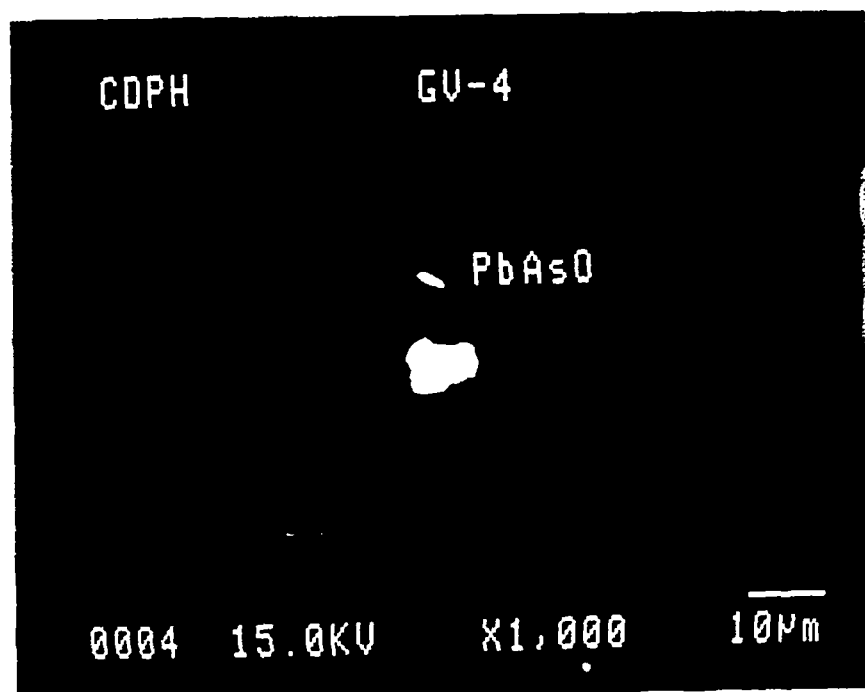


PHOTO 15. EMPA backscatter photomicrographs and EDS x-ray spectra.

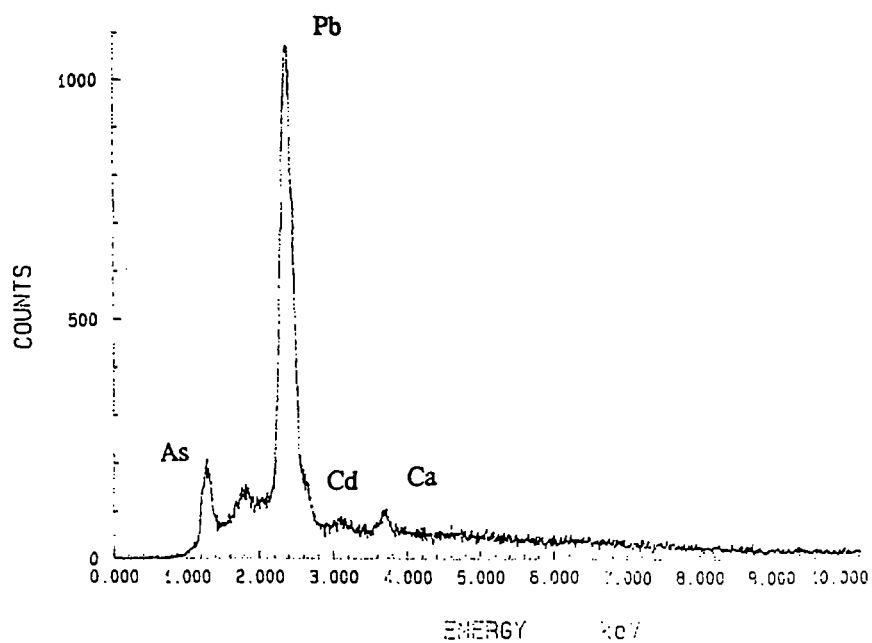
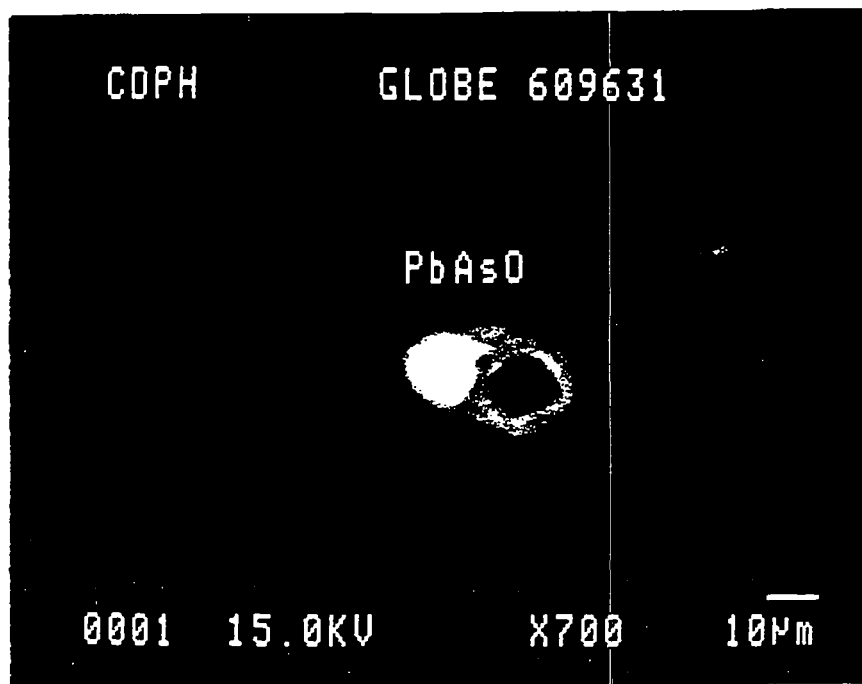


PHOTO 16. EMPA backscatter photomicrographs and EDS x-ray spectra.

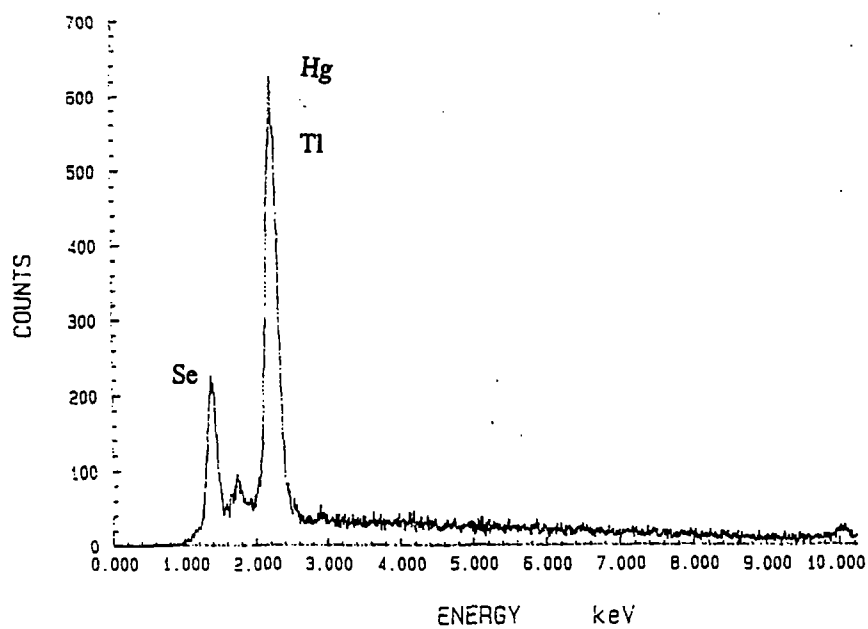
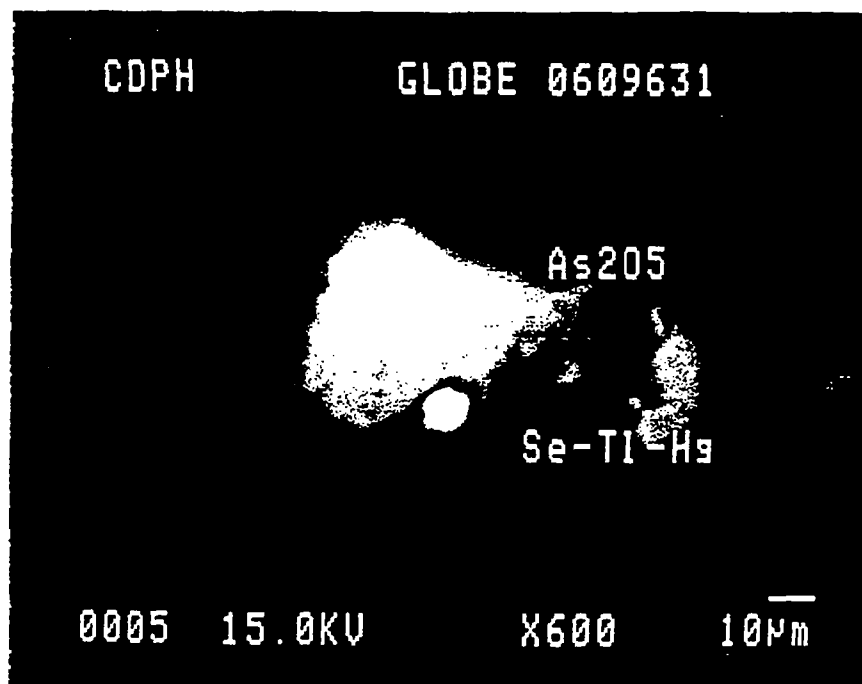


PHOTO 17. EMPA backscatter photomicrographs and EDS x-ray spectra.

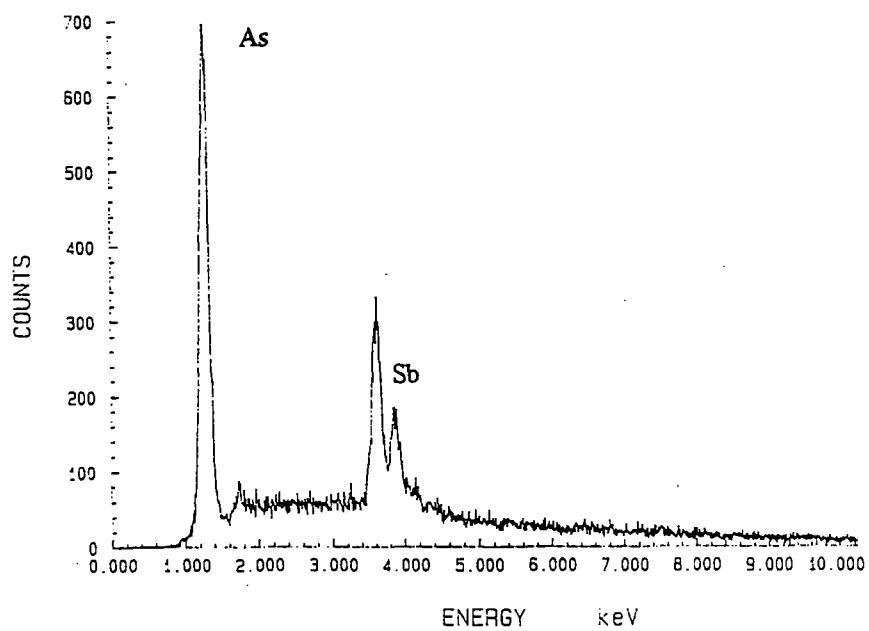
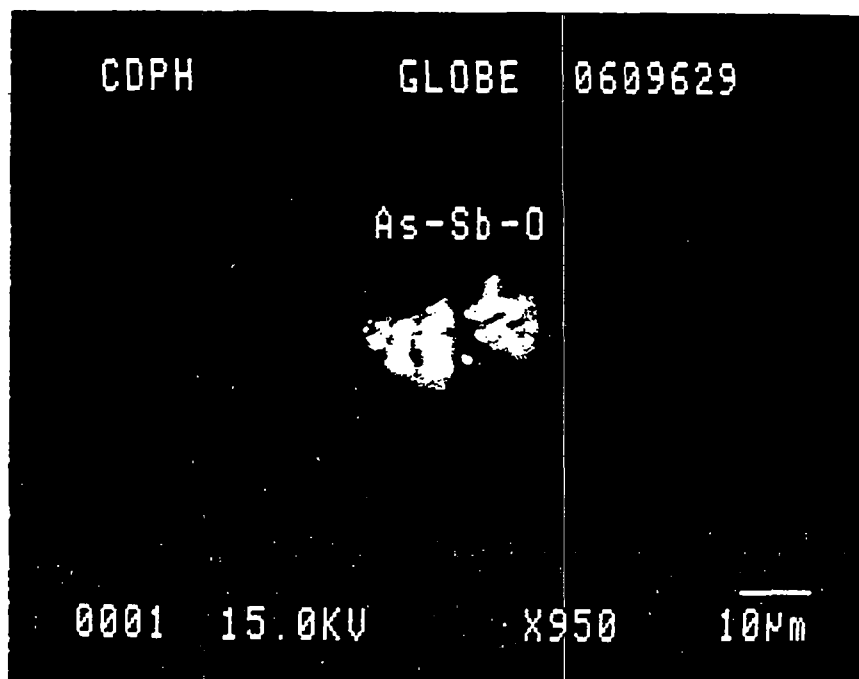


PHOTO 18. EMPA backscatter photomicrographs and EDS x-ray spectra.

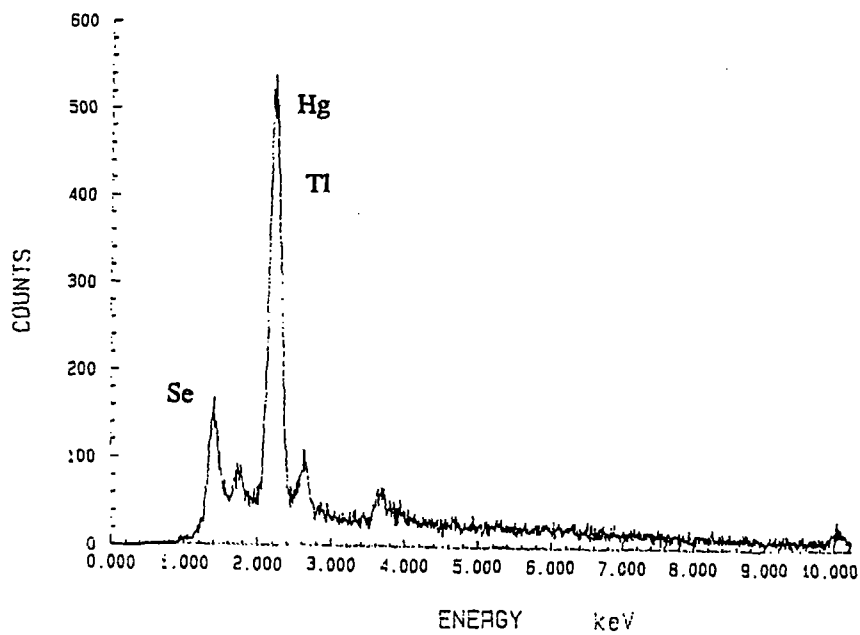
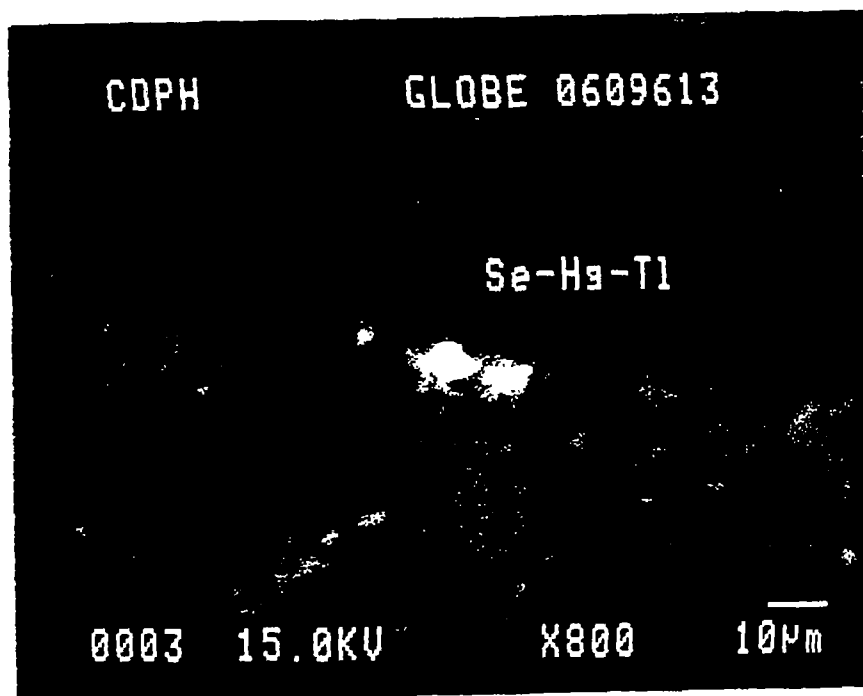


PHOTO 19. EMPA backscatter photomicrograph.

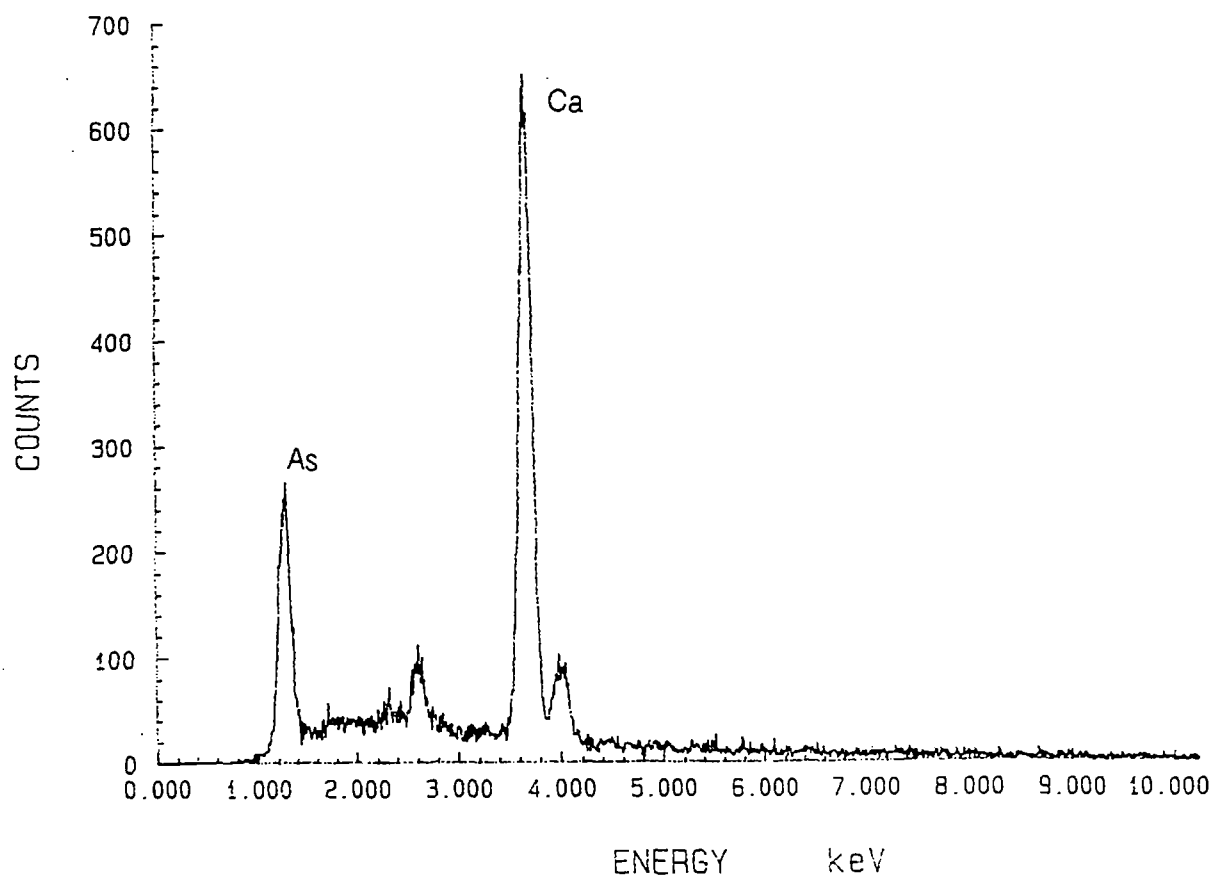
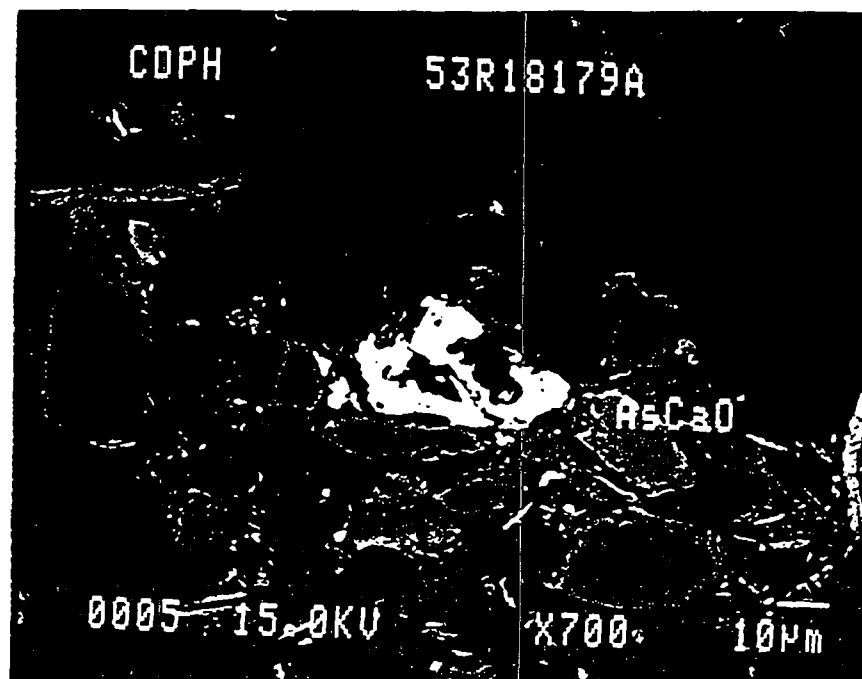


PHOTO 20. EMPA backscatter photomicrograph and EDS x-ray spectra.

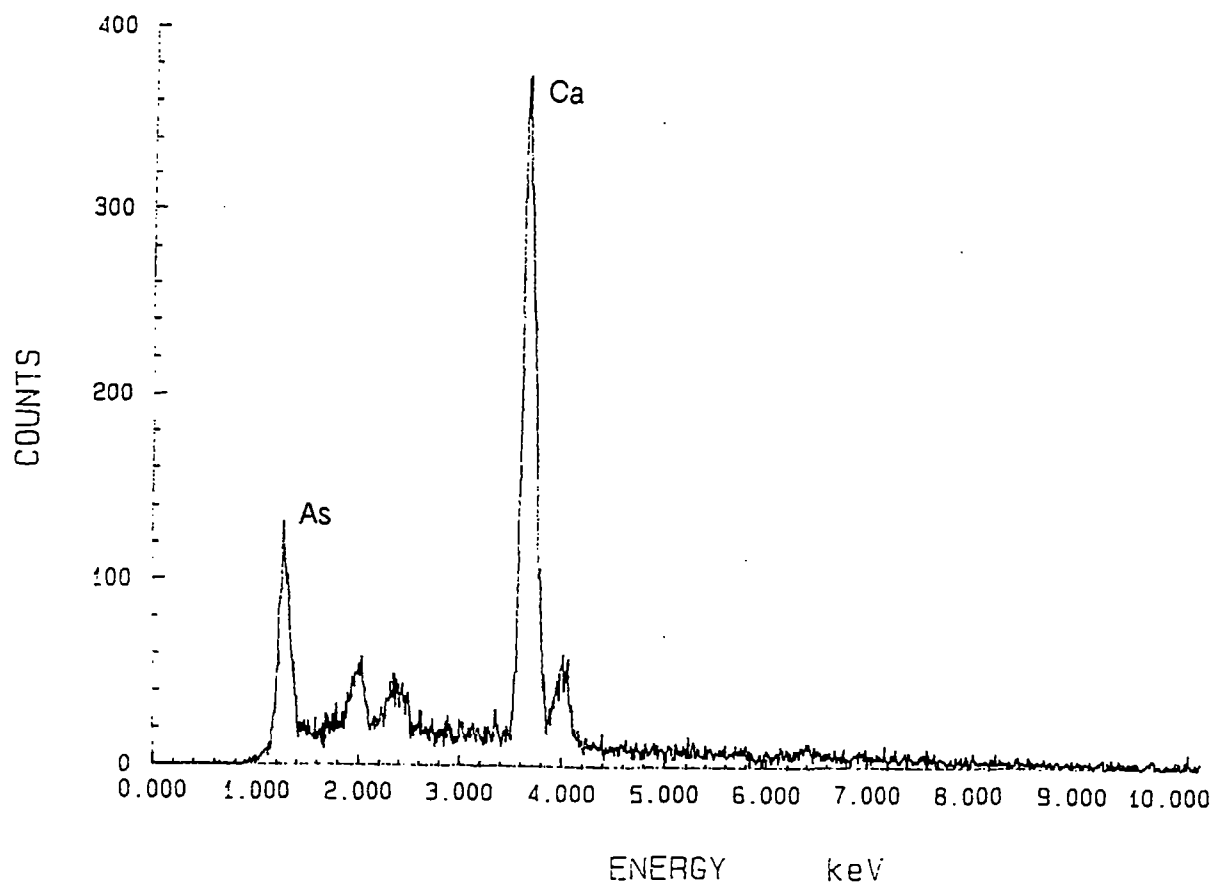
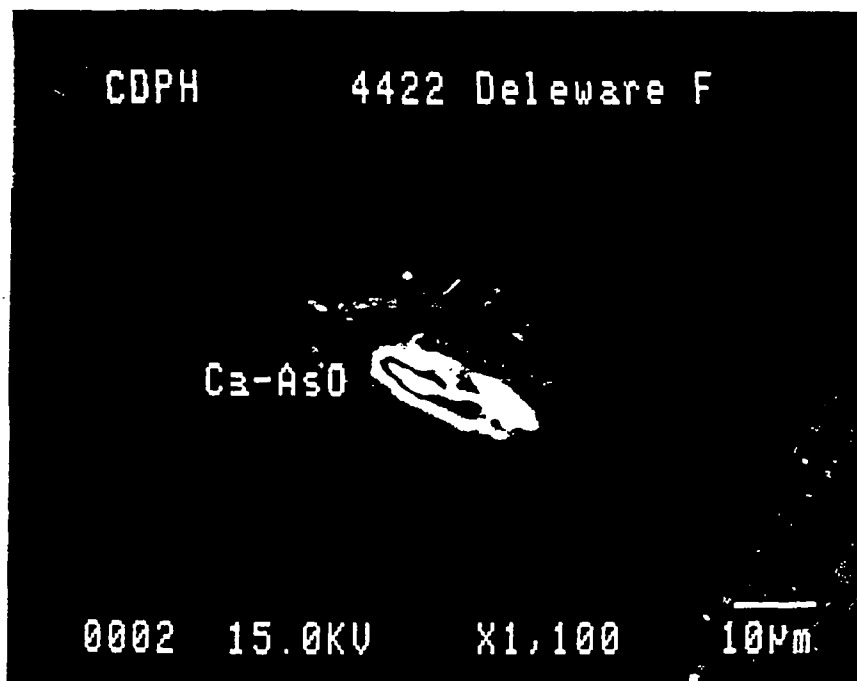


PHOTO 21. EMPA backscatter photomicrograph and EDS x-ray spectra.

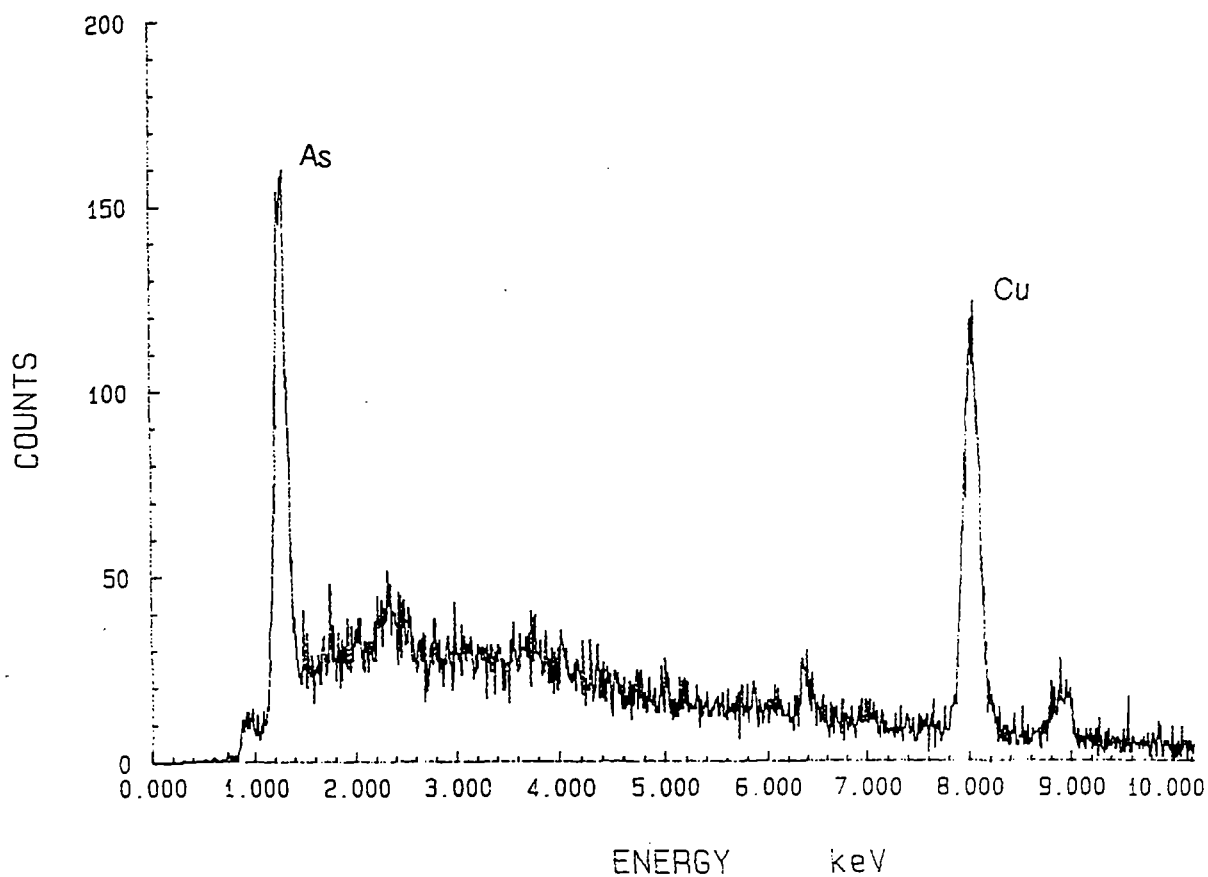
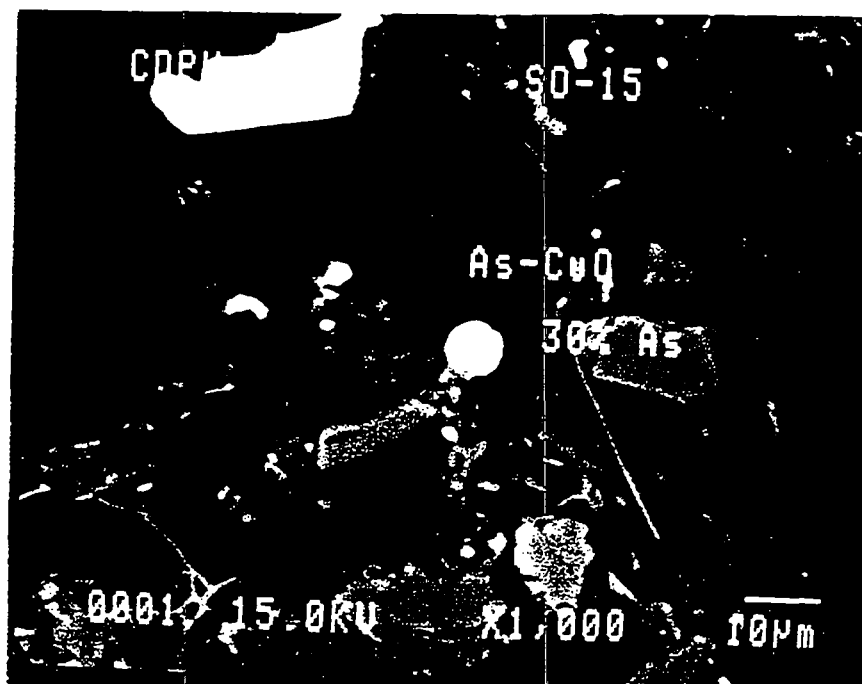


PHOTO 22. EMPA backscatter photomicrograph and EDS x-ray spectra.

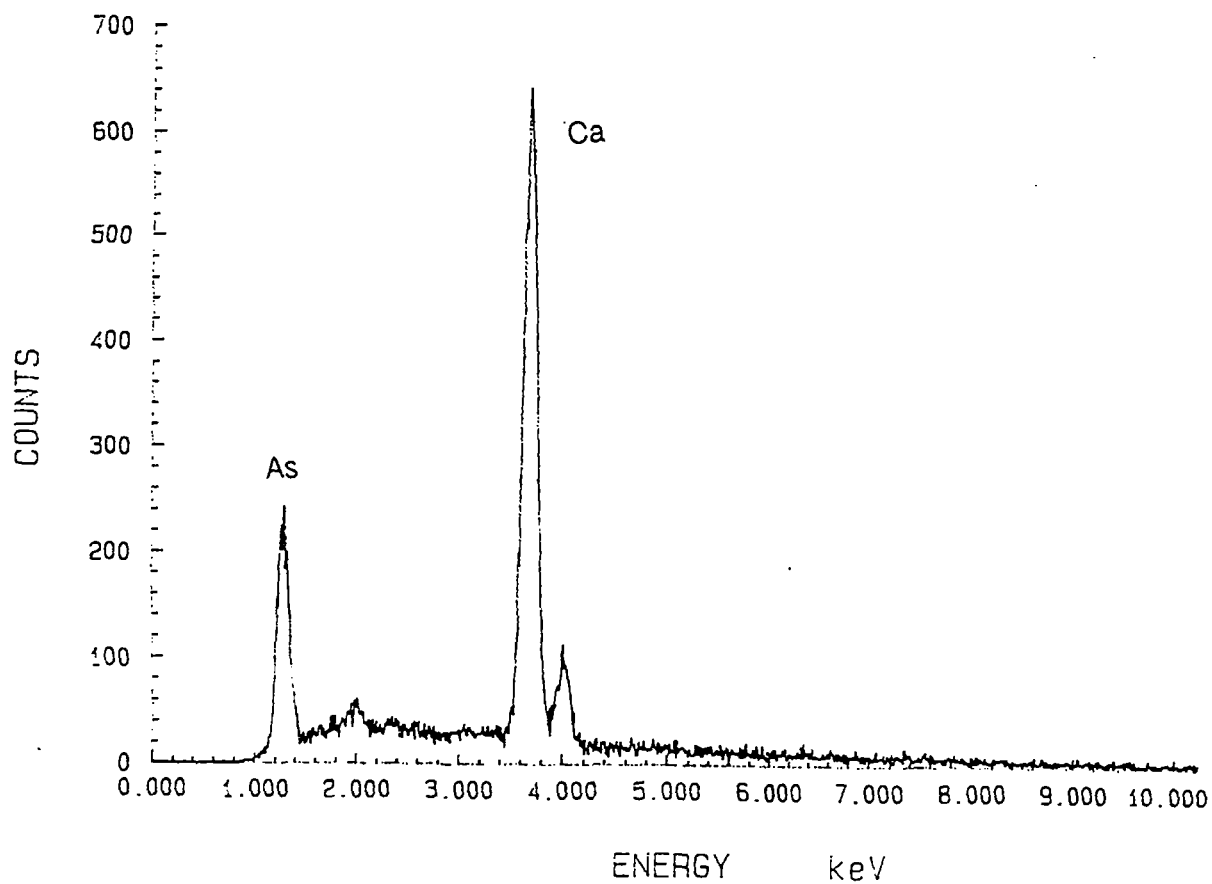
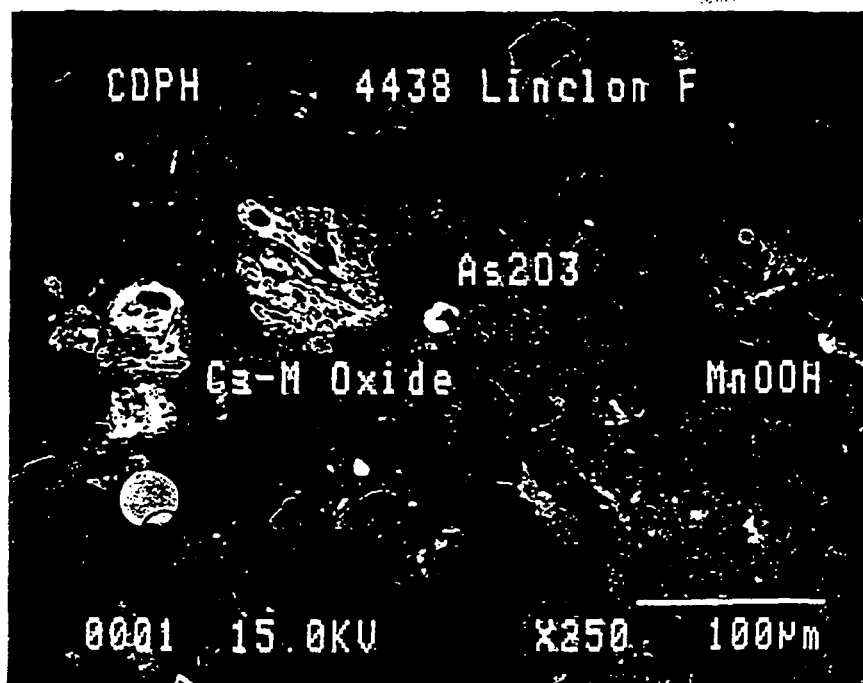


PHOTO 23. EMPA backscatter photomicrograph and EDS x-ray spectra.

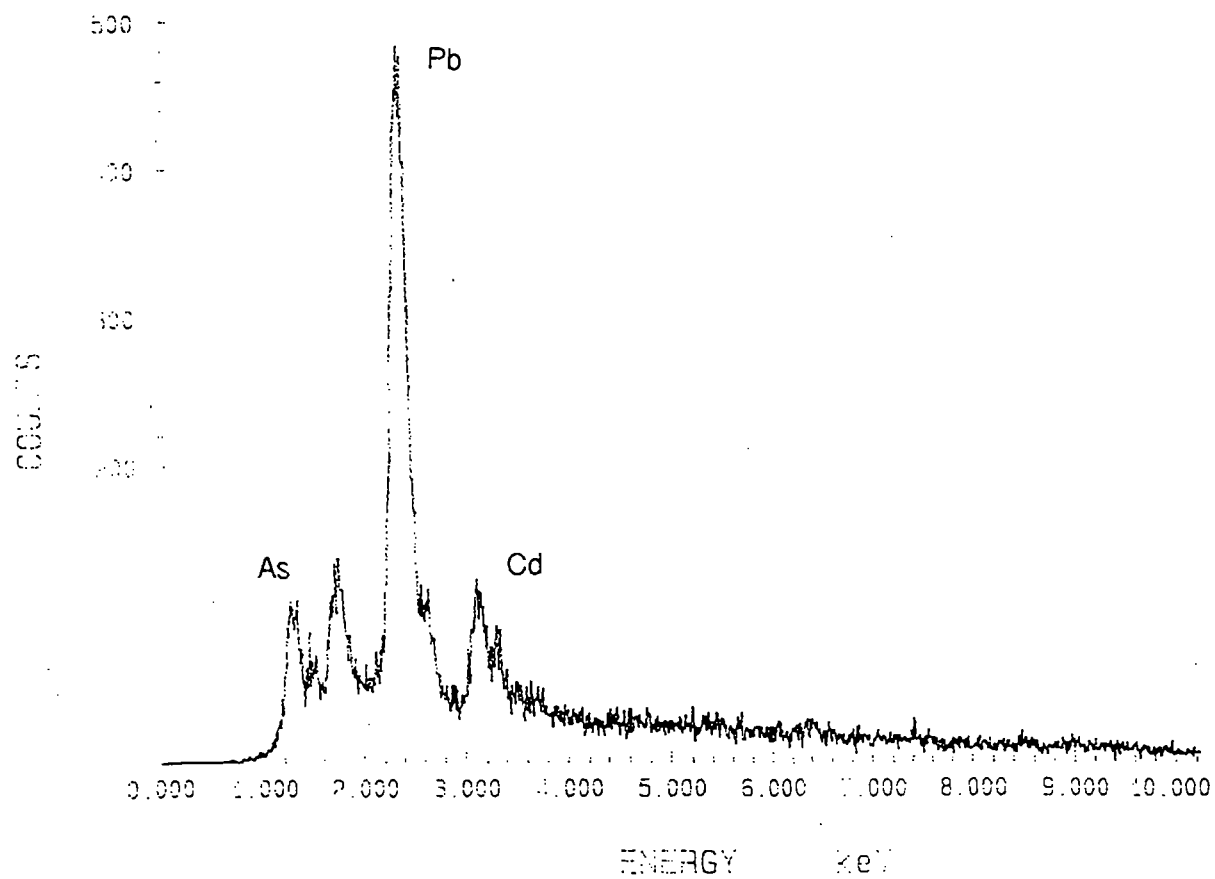


PHOTO 24. EMPA backscatter photomicrograph and EDS x-ray spectra.

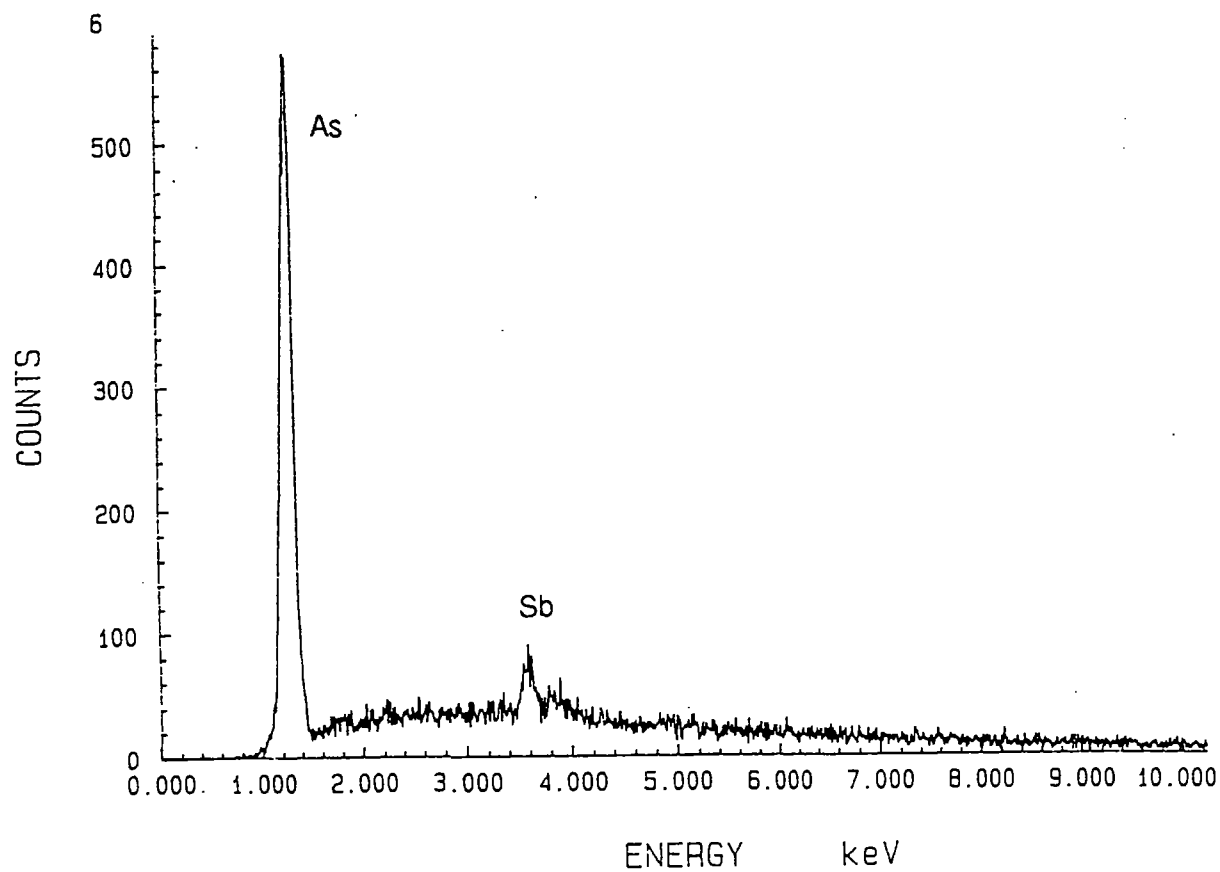
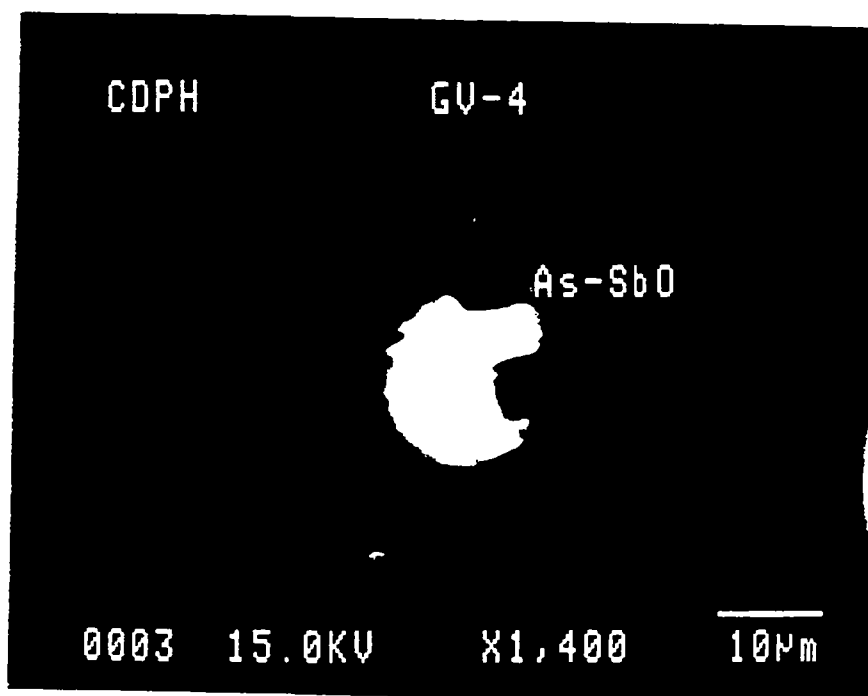


PHOTO 25. EMPA backscatter photomicrograph and EDS x-ray spectra.

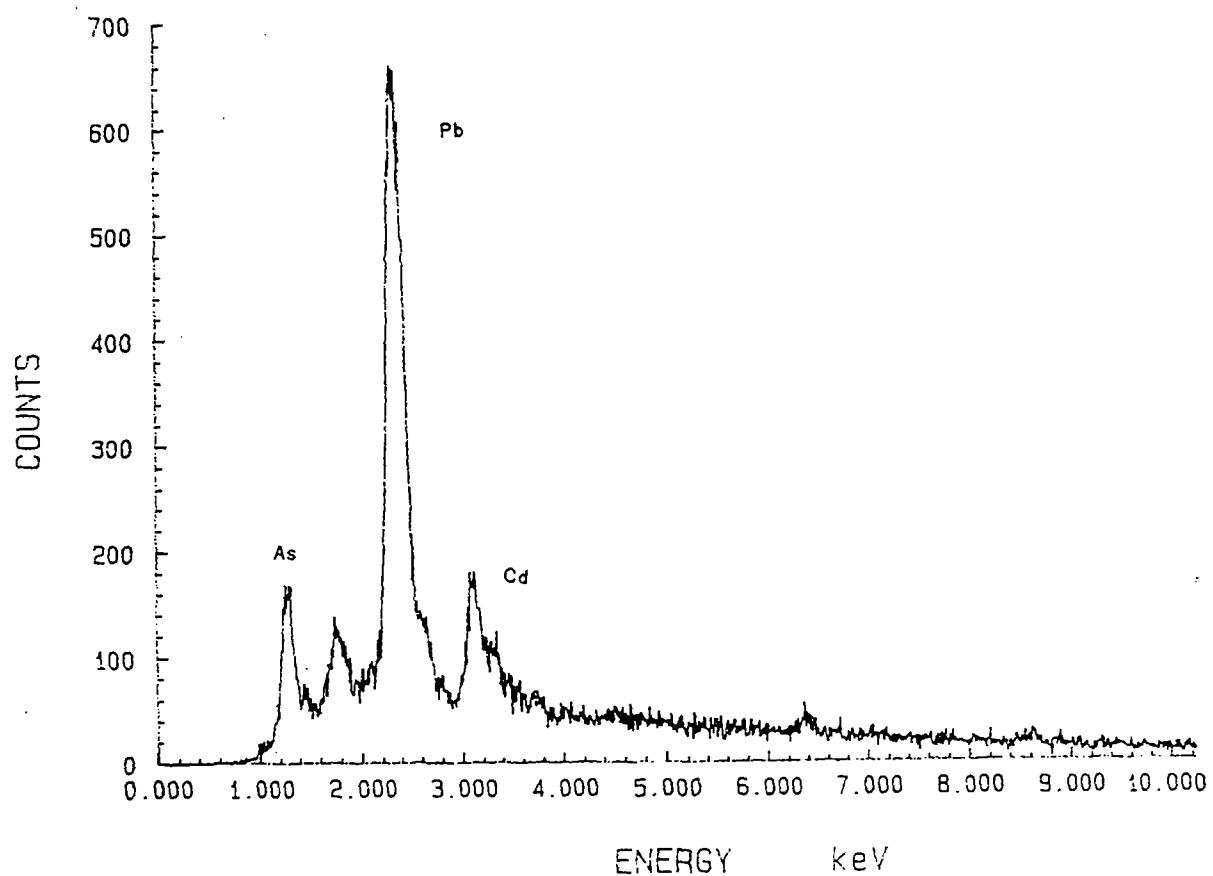
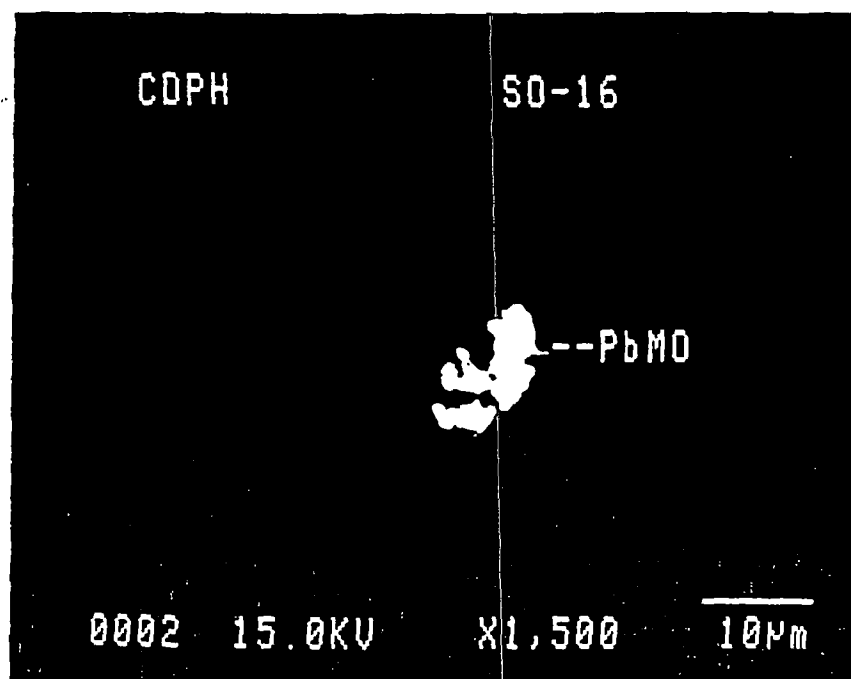
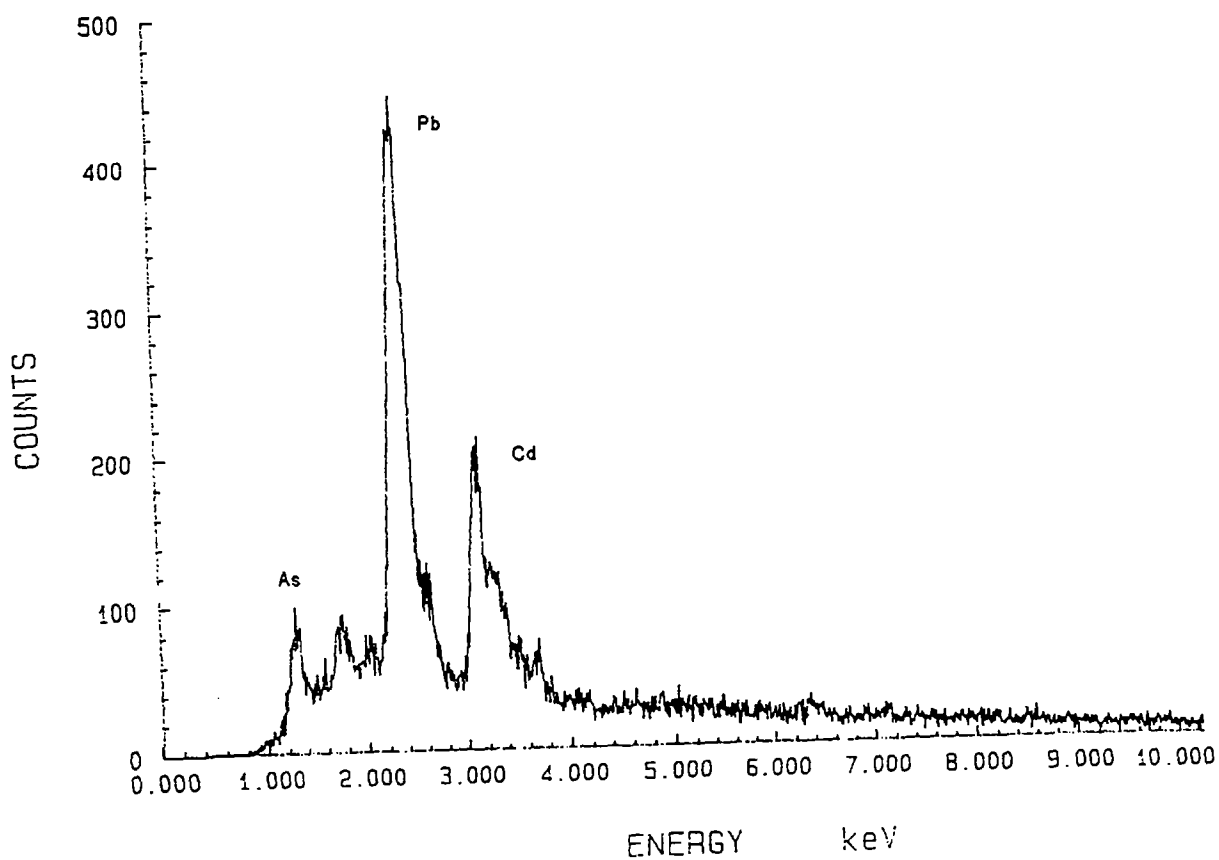
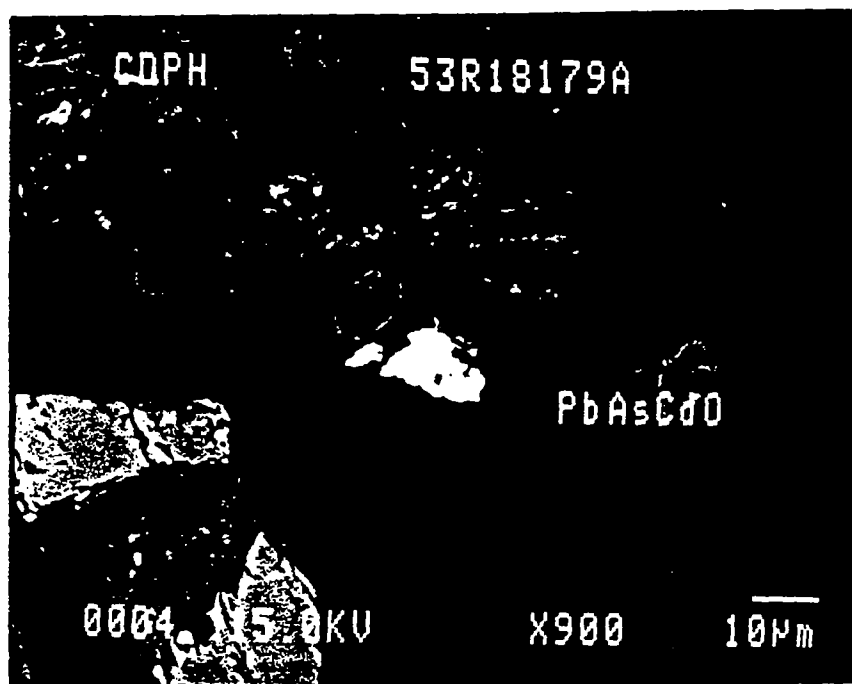


PHOTO 26. EMPA backscatter photomicrograph and EDS x-ray spectra.



Appendix II

EDSXRF LABORATORY METHODS AND QA/QC DATA

A 1.0 INTRODUCTION

A set of solid soil samples were delivered to LEGS (Laboratory for Environmental and Geological Studies) during the months of May through August, 1997 by representatives of Colorado Department of Public Health and Environment (CDPHE). Sample homogeneity and representativeness cannot be evaluated by this laboratory and are the responsibility of CDPHE.

A1.1 Objectives

The goal of this investigation was to provide, at no cost, individuals with data to evaluate the distribution of heavy metals in their residential properties around the historical area known as Globeville, which is located in north Denver, Colorado. This investigation's primary objectives were to determine the concentrations of elements identified as being of potential concern: lead (Pb), arsenic (As), and cadmium (Cd). The EDSXRF analysis was designed to achieve this objective by providing high quality EDSXRF data and QA/QC control.

A 2.0 SAMPLE PREPARATION

A 2.1 Sample Drying

Air drying was necessary to reduce the soil moisture content to a low level to facilitate subsequent splitting and grinding of the samples. All samples were air dried for a minimum of 8 hours at a

temperature of 25 °C. Each sample was placed on a labeled, clean, unused paper plate along with its field label. All plates were covered with a piece of clean computer paper and placed on a drying shelf in a secured area.

A 2.2 Sample Splitting

Sample splitting was designed to create a comparable sub-sample for EDSXRF analyses. Each sample was coned, then divided into four equal segments using a folded piece of clean paper. One segment was removed for further sample preparation, while the remaining material was returned to its original container.

A 2.2 Sample Sieving

The removed segment was then sieved through a 2 mm stainless steel sieve into a stainless steel pan. The < 2 mm fraction remaining in the pan was placed on a clean piece of paper for sample grinding. The sieve and pan were then cleaned by means of compressed air and brush.

A 2.3 Sample Grinding

Grinding was designed to homogenize the sub-sample and reduce the particle size to approximately 350 mesh. Samples were ground using a centrifugal shatter box with tungsten carbide containers.

Sample grinding times were maintained at 2 minutes for all samples. After grinding all of the material was transferred to a clean sheet of computer paper and then to a labeled poly vial.

Between samples each grinding container was carefully cleaned with a nylon brush and Type I water. A sample preparation blank was prepared at a ~10% frequency to monitor any possible contamination caused by sample preparation.

A 3.0 X-RAY FLUORESCENCE ANALYSIS QA/QC

Energy dispersive x-ray fluorescence (EDSXRF) analysis was conducted with a KEVEX 0700 spectrometer following the operating procedures specified in the SOP (LEGS, 1997). The 0700 utilizes a Si-Li detector and a Rh x-ray tube. Secondary targets were used to optimize excitation conditions for a particular element emission line.

A 3.1 EDSXRF Calibration

The EDSXRF instrument was calibrated for the analytes Cd, Pb, and As by defining regions of interest (ROI) using inter-laboratory, NIST SRM and USGS standards. Polynomial regression models were used to relate analyte concentration to analyte ratio value (intensity/compton intensity) for Pb and >100 ppm As. Linear models were used for Cd and <100 ppm As. Calibration curve "r-squared" values range from 0.95-0.99, Figures 3.1-3.3.

A ZAF type correction need not be made to trace element data; however, for major elements this correction should be made for greatest accuracy. In this study only iron has major element concentrations. Since other major elements were not analyzed for, no correction can be made. It is believed this correction would be minor in any case since samples are from similar soil types.

A 3.2 Analytical Technique

EDSXRF analyses were conducted in batches of up to 16 samples. Each batch contained unknown samples, one flux monitor, a preparation blank and a standard. Additionally sample duplicates were analyzed for approximately every other batch. On the average one duplicate was analyzed for every 10 samples. Acquisition conditions (SOP, LEGS,1997) were optimized to achieve the lowest possible detection limits over a reasonable acquisition period.

A 3.2.1 Detection Limits

EDSXRF detection limits were determined using an acceptable procedure (Table A3.2.1).

Experience from past analyses of very large sample populations indicates that the limit of quantification (LOQ), which is the lowest concentration that replication samples have a relative percent difference below 25%, is about 3 times these detection limits.

TABLE A3.2.1 Detection Limits

	As	Pb	Cd
$DL = 2 * S_{(b)}$	20	4	1

$S_{(b)}$ = standard deviation of 7 replicate blanks for As and Pb, 5 blanks for Cd.

A 3.2.2 Procedure Blanks

One procedure blank was prepared for about every 10 field samples analyzed. The procedure blanks were ground using identical conditions to the samples except commercial silica sand was used. The blanks were used to document any contamination that may have occurred during sample preparation. Results of blank analysis are given in Table A3.2.2. The As, Pb and Cd concentrations of all blanks fell within the SOP required levels with the exception of arsenic in Blank 9. It is assumed that this blank indicates minor cross contamination from a prior sample.

Table A 3.2.2 Globeville Preparation Blank Results.

BLANK	As	Pb	Cd
1	2	0	1
2	0	0	2
3	0	0	1
4	3	0	NA
5	0	0	1
9	25	5	2
QTZ-BLANK	19	0	NA
Average	7	1	1
SOP Limits	25	15	15

A 3.2.3 RPD Validations on Duplicates

Duplicates analyses were performed on ~10% of the samples for RPD checks on the elements Pb and As (Table A3.2.3). All samples had acceptable RPDs (<25%) for the element Pb. Only two samples, which have low concentrations of As (<100 ppm), had As RPDs above 25% (GV1 and GV5, Table A3.2.3). Higher RPDs of duplicate samples can be expected as their concentrations approach the detection limit.

A 3.2.4 QA/QC Validation on Standards

NIST SRM MS-2710, MS-2711, and NIST-8607 were used as RPD monitors for all elements. All batches met RPD limits on the three standards (Table A3.2.4.1, Table A3.2.4.2, Table A3.2.4.3, Table A3.2.4.4, Table A3.2.4.5).

A 4.0 FINAL EDSXRF RESULTS

All analyte results from field samples and duplicates are provided in Table A 4.0. About 18% of samples analyzed for arsenic (As) had values below the detection limit of 20 ppm (Table A 3.2.1). All of the samples analyzed for lead (Pb) had values greater than the detection limit for lead (4 ppm). Only one sample result (~2% of sample results) of the samples analyzed for cadmium had a value below the detection limit of 1 ppm.

Table A 3.2.3. Relative Percent Difference (RPD) of duplicate sample analyses.

	As ppm	Pb ppm
GV1	43	154
GV1-DUP	31	172
RPD	32	11
GV5	69	138
GV5-DUP	26	153
RPD	91	10
4428LINCf	355	363
4428LINCfDUP	428	370
RPD	19	2
4438LINCf	2400	792
4438LINCfDUP	2400	783
RPD	0	1
4428LINCR	320	285
4428LINCRDUP	353	319
RPD	10	11
GV4	779	533
GV-4DUP	944	659
RPD	19	21
4715WILL	128	224
4715WILL-D	108	241
RPD	16	7

Table A 3.2.4.1. QAQC validation #1

QAQC Number <u>1</u>		Analyst <u>LUISZER</u>				
Project Number <u>GLOBEVILLE</u>		Analysis date <u>6/12/97</u>				
Sample	As ratio	As ppm	Pb ratio	Pb ppm	Cd rat	Cd
GV1	1.00E-03	33	1.61E-02	154	0.0021	8
GV2	7.64E-04	21	4.73E-02	468	0.0000	1
GV3	9.61E-04	31	1.87E-02	181	0.0013	5
GV4	1.55E-02	779	5.38E-02	533	0.0032	12
GV5	1.62E-03	65	1.45E-02	138	0.0010	4
GV6	5.71E-04	11	1.67E-02	161	0.0014	5
GV6A	5.24E-04	8	1.33E-02	126	0.0006	3
GV7	3.66E-04	0	1.57E-02	151	0.0019	7
BLANK	4.24E-05	0	7.64E-05	0	0.0002	1
MS2710	1.31E-02	655	5.49E-01	5000	0.0053	20
MS2711	1.98E-03	83	1.08E-01	1100	0.0117	43
GV1-DUP	7.21E-04	18	1.78E-02	172	0.0023	9
GV5-DUP	6.09E-04	13	1.59E-02	153	0.0012	5
MS2710	1.31E-02	655	5.49E-01	5000	0.0053	20
RPD (NIST-2710)		4		10		11
Monitor ratio	1.2632		1.2632			


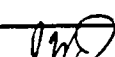
QA/QC	Passed 
	Failed
	Validated 

Table A 3.2.4.2. QAQC validation #2

QAQC Number 2		Analyst LUISZER				
Project Number GLOBEVILLE		Analysis date 12-Jul-97				
Sample	As ratio	As ppm	Pb ratio	Pb ppm	Cd rat	Cd
4363LINCR	1.89E-03	79	2.57E-02	251	1.46E-03	6
4460PENNF	4.25E-03	200	7.52E-02	744	3.54E-03	13
4460PENNR	8.96E-03	441	4.44E-02	439	3.21E-03	12
4438LINCB	1.48E-02	742	5.31E-02	526	3.63E-03	14
4428LINCR	7.08E-03	345	3.14E-02	309	2.01E-03	8
4428LINCf	9.31E-03	459	3.81E-02	376	3.48E-03	13
4425PENNR	1.80E-04	0	3.68E-02	363	9.45E-04	4
GV-8F	8.42E-04	25	2.04E-02	198	1.58E-03	6
BLANK	0.00E+00	0	1.31E-04	0	2.83E-04	2
4363LINCf	1.62E-03	65	2.43E-02	237	2.32E-03	9
4432LINCB	1.21E-03	44	3.34E-02	329	2.66E-03	10
4438LINCf	4.40E-02	2200	7.48E-02	741	4.67E-03	17
4425PENNF	1.00E-03	33	2.15E-02	210	1.47E-03	6
4432LINCf	4.14E-04	3	3.47E-02	342	2.01E-03	8
MS2710	1.50E-02	750	6.13E-01	5500	5.23E-03	19
RPD (NIST-2710)		18		1		12
Monitor ratio	1.1676		1.1676		0.6631	

QA/QC	
Passed	<input checked="" type="checkbox"/>
Failed	<input type="checkbox"/>
Validated	<i>JND</i>

Table A 3.2.4.3. QAQC validation #3

QAQC Number		3		Analyst		Luiszer	
Project Number		GLOBEVILLE		Analysis date		29-Jul-97	
Sample	As ratio	As ppm	Pb ratio	Pb ppm	Cd ratio	Cd ppm	
4650 Williams SO-09	5.22E-04	8	2.25E-02	219	7.38E-04	3.2	
4815 St. Pauls SO-01	2.44E-03	107	1.36E-02	130	7.93E-04	3.4	
4643 Williams SO-08	2.37E-04	0	2.89E-02	284	1.63E-03	6.4	
BLANK-2	0.00E+00	0	0.00E+00	0	1.73E-04	1.1	
4674 Williams SO-06	6.95E-04	17	2.35E-02	230	1.59E-03	6.2	
4680 Williams SO-05	3.64E-04	0	4.00E-02	395	1.07E-03	4.4	
4770 Vine SO-17	1.58E-04	0	3.93E-02	388	1.34E-03	5.3	
4784 Gaylord SO-24	1.18E-03	42	2.57E-02	252	1.35E-03	5.4	
4747 Williams SO-12	6.27E-04	13	2.34E-02	228	1.35E-03	5.4	
4631 Franklin SO-03	4.44E-04	4	5.07E-02	502	9.60E-04	4.0	
4709 Race SO-14	1.75E-03	71	3.32E-02	327	1.58E-03	6.2	
4770 Fillmore SO-02	9.24E-04	29	4.65E-03	39	9.23E-04	3.8	
4659 Williams SO-07	2.17E-03	93	4.42E-02	437	1.80E-03	7.0	
4629 Vine SO-23	3.63E-04	0	3.23E-02	318	9.69E-04	4.0	
MS2710	1.47E-02	735	6.23E-01	5600	5.14E-03	19.0	
RPD (NIST-2710)		16		1		14	
Monitor ratio	1.1446		1.1446		0.6551		
QA/QC							
Passed		✓					
Failed							
Validated		J h Q					

Table A 3.2.4.4. QA/QC validation #4

QA/QC Number	4		Analyst LUISZER	
Project Number	Globeville		Analysis date 6-Aug-97	
Sample	As ratio	As ppm	Pb ratio	Pb ppm
4460PENNR	9.20E-03	454	4.27E-02	422
4428LINCf	7.27E-03	355	3.68E-02	363
4438LINCB	1.35E-02	677	5.11E-02	506
4438LINCf	4.83E-02	2400	8.00E-02	792
4428LINCR	6.59E-03	320	2.91E-02	285
4718RACE	3.80E-02	1900	8.86E-02	876
BLANK	6.66E-05	0	1.90E-05	0
4428LINCfDUP	8.70E-03	428	3.75E-02	370
4438LINCfDUP	4.86E-02	2400	7.91E-02	783
4428LINCRDUP	7.23E-03	353	3.24E-02	319
GV-4DUP	1.88E-02	944	6.66E-02	659
MS-2711	2.11E-03	90	1.28E-01	1300
QTZ-BLANK	4.56E-04	5	2.57E-04	0
MS2710	1.56E-02	783	6.76E-01	6000
RPD (NIST-2710)		22		8
Monitor ratio	1.1411		1.1411	

QA/QC	
Passed	<input checked="" type="checkbox"/>
Failed	<input type="checkbox"/>
Validated	<i>[Signature]</i>

Table A 3.2.4.5. QAQC validation #5

QAQC Number <u>5</u>		Analyst <u>Luiszer</u>				
Project Number <u>GLOBEVILLE</u>		Analysis date <u>16-Aug-97</u>				
Sample	As ratio	As ppm	Pb ratio	Pb ppm	Cd ratio	Cd ppm
BLANK-9	5.83E-04	11	1.34E-03	5	3.74E-04	2
3638 Delgany-B	5.76E-04	11	3.55E-02	350	1.60E-03	6
3638 Delgany-F	7.44E-04	20	3.01E-02	296	8.64E-04	4
3638 Delgany-G	4.64E-04	5	6.25E-02	619	1.09E-03	4
4352 Cherokee-F	8.80E-04	27	2.27E-02	221	8.49E-04	4
4352 Cherokee-R	5.49E-04	10	5.40E-02	534	1.70E-03	7
4422 Delaware-G	2.58E-03	114	3.65E-02	360	2.22E-03	9
4422 Delaware-F	3.01E-03	136	5.35E-02	529	1.69E-03	7
4469 Cherokee-B	1.42E-03	54	3.11E-02	306	6.64E-04	3
4470 Cherokee-F	1.28E-03	47	3.68E-02	363	1.20E-03	5
4474 Cherokee-F	3.49E-04	0	2.27E-02	221	6.12E-04	3
4474 Cherokee-S	1.04E-03	35	1.27E-02	120	1.20E-03	5
NIST-8607	3.45E-02	1700	2.28E-01	2200	6.83E-03	25
RPD (NIST-8607)		6		17		4
Monitor ratio	1.0843		1.0843		0.6236	
QA/QC						
Passed		<input checked="" type="checkbox"/>				
Failed		<input type="checkbox"/>				
Validated		<input checked="" type="checkbox"/>				

Table A4.0. Final EDSXRF Analytical results of samples and sample duplicates.

	Sample	As ppm *	Pb ppm	Cd ppm
	3638 Delgany-B	25	350	6
	3638 Delgany-F	32	296	4
	3638 Delgany-G	20	619	4
	4352 Cherokee-F	38	221	4
	4352 Cherokee-R	23	534	7
	4363LINCf	69	237	9
	4363LINCR	81	251	6
	4422 Delaware-F	136	529	7
	4422 Delaware-G	114	360	9
	4425PENNF	43	210	6
	4425PENNR	8	363	4
	4428LINCf	459	376	13
	4428LINCf	355	363	NA
	4428LINCfDUP	428	370	NA
	4428LINCR	345	309	8
	4428LINCR	320	285	NA
	4428LINCRDUP	353	319	NA
	4432LINCB	52	329	10
	4432LINCf	18	342	8
	4438LINCB	742	526	14
	4438LINCB	677	506	NA
	4438LINCf	2200	741	17
	4438LINCf	2400	792	NA
	4438LINCfDUP	2400	783	NA
	4460PENNF	200	744	13
	4460PENNR	441	439	12
	4460PENNR	454	422	NA
	4469 Cherokee-B	61	306	3
	4470 Cherokee-F	55	363	5
	4474 Cherokee-F	15	221	3
	4474 Cherokee-S	44	120	5
	4718RACE	1900	876	NA
	GV-4DUP	944	659	NA
	GV-8F	36	198	6
	GV-1	43	154	8
	GV-1-DUP	31	172	9
	GV-2	33	468	1
	GV-3	41	181	5
	GV-4	779	533	12
	GV-5	69	138	4
	GV-5-DUP	26	153	5
	GV-6	24	161	5
	GV-6A	22	126	3
	GV-7	16	151	7
4815 St. Pauls	SO-01	107	130	3
4770 Fillmore	SO-02	39	39	4
4631 Franklin	SO-03	19	502	4
4680 Williams	SO-05	16	395	4

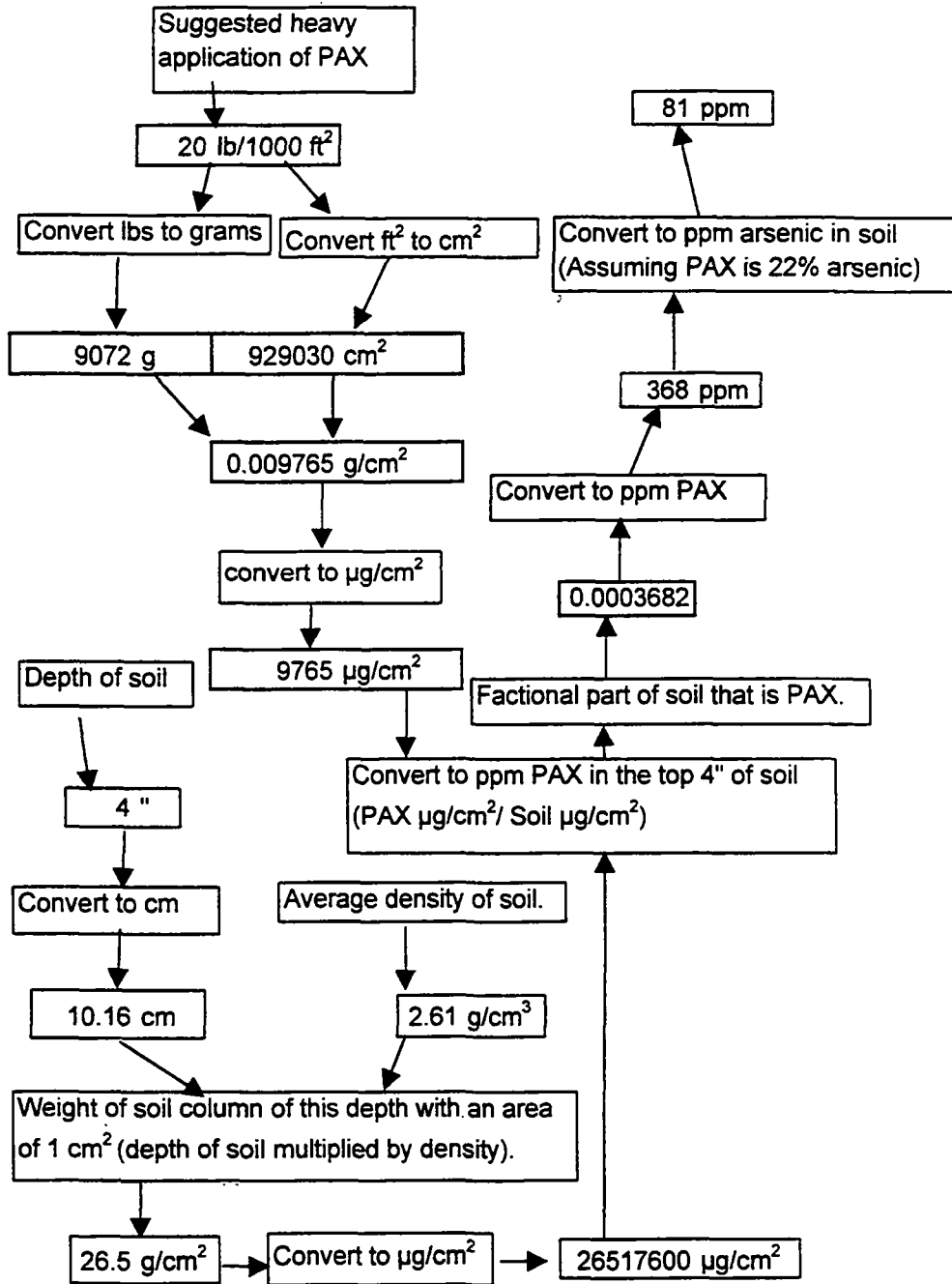
	Sample	As ppm *	Pb ppm	Cd ppm
4674 Williams	SO-06	30	230	6
4659 Williams	SO-07	93	437	7
4643 Williams	SO-08	10	284	6
4650 Williams	SO-09	22	219	3
4747 Williams	SO-12	27	228	5
4709 Race	SO-14	75	327	6
4770 Vine	SO-17	7	388	5
4629 Vine	SO-23	16	318	4
4784 Gaylord	SO-24	50	252	5

*Arsenic values <100 vary slightly from initial QA-QC sheets because a final linear calibration was utilized to enable the comparison of EDSXRF results with ICP results.

NA = Not Analyzed.

computation

Flowchart showing calculation of arsenic concentration in top 4" of soil from the application of the suggested heavy application of PAX.



APPENDIX II

SPECIATION SOP

METAL SPECIATION STANDARD OPERATING PROCEDURE

February 10, 1995

PREPARED BY

University of Colorado

Department of Geological Sciences

Laboratory For Environmental and Geological Studies

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Appendix A- Health and Safety

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1.0 OBJECTIVES

The objectives of this Standard Operating Procedure (SOP) are to identify the proper methodologies and protocols to be used during metal speciation of mine-related waste samples (including; tailings, slags, sediments, dross, bag house dusts, and paint), residential soils and dusts for lead, arsenic, cadmium, copper, or zinc. The metal speciation data generated from this SOP may be used to assess bioaccessability as it relates to risk. Parameters identified during the speciation analyses that are used to quantify bioaccessability include; particle size, associations, stoichiometry, frequency of occurrence of metal-bearing forms and relative mass of metal-bearing forms. This electron microprobe technique (EMPA) along with instrument operation protocols, and sample preparation to be used during implementation of the Metals Speciation SOP are discussed in the following sections.

2.0 BACKGROUND

To date numerous metal-bearing forms have been identified from various environments within western mining districts, Table 2.1 (Emmons et al., 1927, Drexler, 1991 per. comm., Drexler, 1992, Davis et al., 1993; Ruby et al., 1994, CDM, 1994, Weston, 1995). This listing does not preclude the identification of other metal-bearing forms, but only serves as an initial point of reference. Many of these forms represent a series of minerals with varying metal concentrations (eg. lead phosphate, Fe-Pb oxide, Mn-Pb oxide, and slag). Since limited thermodynamic information is available for many of these phases and equilibrium conditions are rarely found in soil environments, the identity of the mineral class (eg. lead phosphate) will be sufficient and exact stoichiometry is not necessary.

It is important to know the particle-size distribution of metal-bearing forms in order to assess potential risk. It is believed that particles less than 250 μm (microns) are most available for human

ingestion and/or inhalation (Bornshine, et al., 1987). For this study the largest dimension of any one metal-bearing form will be measured and the frequency of occurrence weighted by that dimension. Although not routinely performed, particle area can be determined. It has been shown (CDM, 1994) that this data produces similar results and area measurements only serve to add a considerable amount of time to the procedure thus limiting the total number of particles or samples that can be observed in a study.

Mineral associations may have profound effects on metal bioaccessability. For example; if a lead-bearing form in one sample is predominantly found within quartz grains while in another sample it is free in the sample matrix the two samples are likely to pose significantly different risk levels to human health. Therefore, associations of concern include the following:

- 1) free or liberated
- 2) inclusions within a second phase
- 3) cementing or encrusting-rimming

TABLE 2.1 Metal-bearing forms found within western mining districts.

OXIDES

Lead oxide
Manganese metal* oxide
Iron metal oxide
Lead molybdenum oxide
Arsenic oxide
Cadmium oxide
Copper oxide
Zinc oxide

SILICATES

Slag
Lead silicate
Arsenic silicate
Zinc silicate
Clays

SULFATES

Iron metal sulfate
Lead sulfate
Lead barite
Zinc sulfate
Arsenic sulfate
Copper sulfate

CARBONATES

Lead carbonate
Zinc carbonate

PHOSPHATES

Metal phosphates

SULFIDES

Lead sulfide
Sulfosalts
Iron-arsenic sulfide
Zinc sulfide
Copper sulfides
Copper-iron sulfide

METALLIC Lead, Zinc, Copper, Cadmium
Lead/Arsenic/Cadmium chlorides
Lead paint
Solder
Metal organic
Lead vanadate

Minor telluride, and bismuth-lead phases

* The reference to "metal" refers to sorbed Pb, Cu, Zn, Cd, or As.

3.0 SAMPLE SELECTION

Samples should initially be selected based on available site characteristics. Additional samples may be collected if field investigations reveal new source areas. The element to be speciated (Pb, As, Cu, Zn or Cd) should be selected based on overall risk and initial bulk chemical analyses. The methods and conditions of sample selection, collection, preservation, and representativeness are the responsibility of the CDPHE.

4.0 SCHEDULE

A schedule for completion of projects performed under the Metals Speciation SOP will be provided in writing or verbally to the contractor along with monthly reporting requirements if large projects are performed. These schedules are based on an aggressive analytical program designed to ensure that the metals speciation analyses are completed in a timely period. Monthly reports are expected to reflect schedule status.

5.0 INSTRUMENTATION

Speciation analyses will be conducted at the Laboratory for Environmental and Geological Studies at the University of Colorado, Boulder. Primary equipment used for this work will include:

Electron Microprobe (JEOL 8600) equipped with four wavelength spectrometers, energy dispersive spectrometer (EDS), BEI detector and the TN- 5600 data processing system. Geller dPIC hardware and software for image storage and processing. An LEDC spectrometer crystal for carbon and LDE-1 crystal for oxygen analyses will be used.

6.0 PRECISION and ACCURACY

The precision of the EMPA speciation will be evaluated based on sample duplicates analyzed at intervals of 10%, if more than 10 samples are run. The accuracy of the analyses will be estimated based on a number of methods depending on the source of the data. Data generated by the "EMPA point count" will be evaluated statistically based on the method of Mosimann (1965) at the 95% confidence level. It is very important that every attempt be made to insure that a minimum of 100-200 total particles are counted in order to provide a statistically meaningful particle count. If the contractor specifies, either the NIST 2710 or 2711 "Montana soils" can be speciated for traceability.

Quantitative elemental analysis, primarily performed on slag or other variable, metal-bearing forms, will have precision and accuracy evaluated on counting statistics and reproducibility of NIST or other certified standards using conventional EMPA methods. In general, site-specific concentrations for these variable, metal-bearing forms will be determined and compiled, Table A6.0. Average concentrations will then be used for further calculations. Data on specific gravity will be collected from referenced data bases or estimated based on similar compounds.

7.0 PERSONNEL RESPONSIBILITY

The analysts will carefully read the standard operating procedure prior to any sample examination.

It is the responsibility of the lab supervisor and designates to ensure that these procedures are followed, to examine QA and replicate standards, and to check EDS and WDS calibrations. The laboratory supervisor will collect results, ensure they are in proper format, and deliver them to the CDPHE.

Monthly reports summarizing all progress, with a list of samples speciated to date with data analyses

TABLE A8.0. Site-Specific Data Used for Relative Arsenic Mass Calculations.

	As2O3	As4O6	PbAsO	FE	MN	PHOS	SLAG	SULF	FE-ASO	Al-ASO	CLAY	CA-ASO	CA-SIO	PBMO	Solder	AsSbO	Sulfosalt	Arsenopyrite
Specific Gravity	3.9	7.1	7.7	4	5	5	3.6	3.7	4.2	3.4	3.1	3.6	3.6	7.1	6.3	4.6	4.4	6
AVERAGE	66.06095	10.24444	10.1	1.364233	0.779867	0.998118	0.166571	1.7385	23.43333	24.53333	0.831	24.23333	16.4775	2.93				
ST.DEV	5.072063	4.928455	3.36353	1.788272	1.965032	1.7131	0.216153	1.943124	0.51316	3.617089	1.190098	1.885382	1.53602	4.242726				
ZAF CORRECTED PPM	757400	150000	150000	27000	15000	15000	3200	34000	460000	250000	8300	360000	240000	45000	250		190000	460000

sheets (DAS) will be submitted each month.

It is also the responsibility of the laboratory supervisor to notify the CDPHE representative, of any problems encountered in the sample analysis procedure.

8.0 METHODOLOGY

8.1 SAMPLE PREPARATION

The minus 250 μm size fraction of sample will be used for metal speciation. Grain mounts, 1.5 inches in diameter, of each sample will be prepared using air-cured epoxy. The grain mounting procedure involves the following:

- 1) Logging the samples of which polished mounts will be prepared
- 2) Inspection of all plastic cups, making sure each is clean and dry
- 3) Labeling each "mold" with its corresponding sample number.
- 4) All samples will be split to produce a homogeneous 1-4 gram sample.
- 5) Mixing epoxy resin and hardener according to manufacturer's directions.
- 6) Pour 1 gram of sample into mold. Double checking to make sure sample numbers on mold and sample match. Pouring epoxy into mold to just cover sample grains.
- 7) Using a new wood stirring stick with each sample, carefully blend epoxy and grains so as to coat all grains with epoxy.
- 8) Setting molds to cure at ROOM TEMPERATURE in a clean restricted area. Adding labels with sample numbers and covering with more epoxy resin. Leaving to cure completely at room temperature.
- 9) One at a time, removing each sample from its mold and grinding flat the back side of the mount.
- 10) Using 600 grit wet abrasive paper stretched across a grinding wheel for removing the bottom layer and exposing as many mineral grains as possible. Follow with 1000 grit paper.
- 11) Start polishing with 15 μm oil based diamond paste on a polishing paper fixed to a lap. Using paper instead of cloth minimizes relief.

12) Next use 6 μm diamond polish on a similar lap.

13) Finally polish the sample with 1 μm oil based diamond past on polishing paper. Followed by .05 μm alumina in water suspension. The quality should be checked after each step. Typical polishing times are 30 minutes for 15 μm , 20 minutes for 6 μm , 15 minutes for 1 μm and 10 minutes for 0.05 μm .

NOTE: use low speed on the polishing laps to avoid "plucking"
of sample grains.

14) Samples should be completely cleaned in an ultrasonic cleaner with isopropyl alcohol or similar solvent to remove oil and finger prints.

15) To insure that no particles of lead are being cross contaminated with sample preparation procedures, a blank (epoxy only) mold will be made every 50th sample following all of the above procedures. This mold will then be speciated along with the other samples.

16) Each sample be carbon coated. Once coated the samples should be stored in a clean, dry environment with the carbon surface protected from scratches or handling.

8.2 POINT COUNTING

Counts are made by traversing each sample from left-to-right and top-to-bottom as illustrated in Figure 8.1. The amount of vertical movement for each traverse would depend on magnification and CRT (cathode-ray tube) size. This movement should be minimized so that NO portion of the sample is missed when the end of a traverse is reached. Two magnification settings generally are used. One ranging from 40-100X and a second from 300-600X. The last setting will allow one to find the smallest identifiable (1-2 micron) phases.

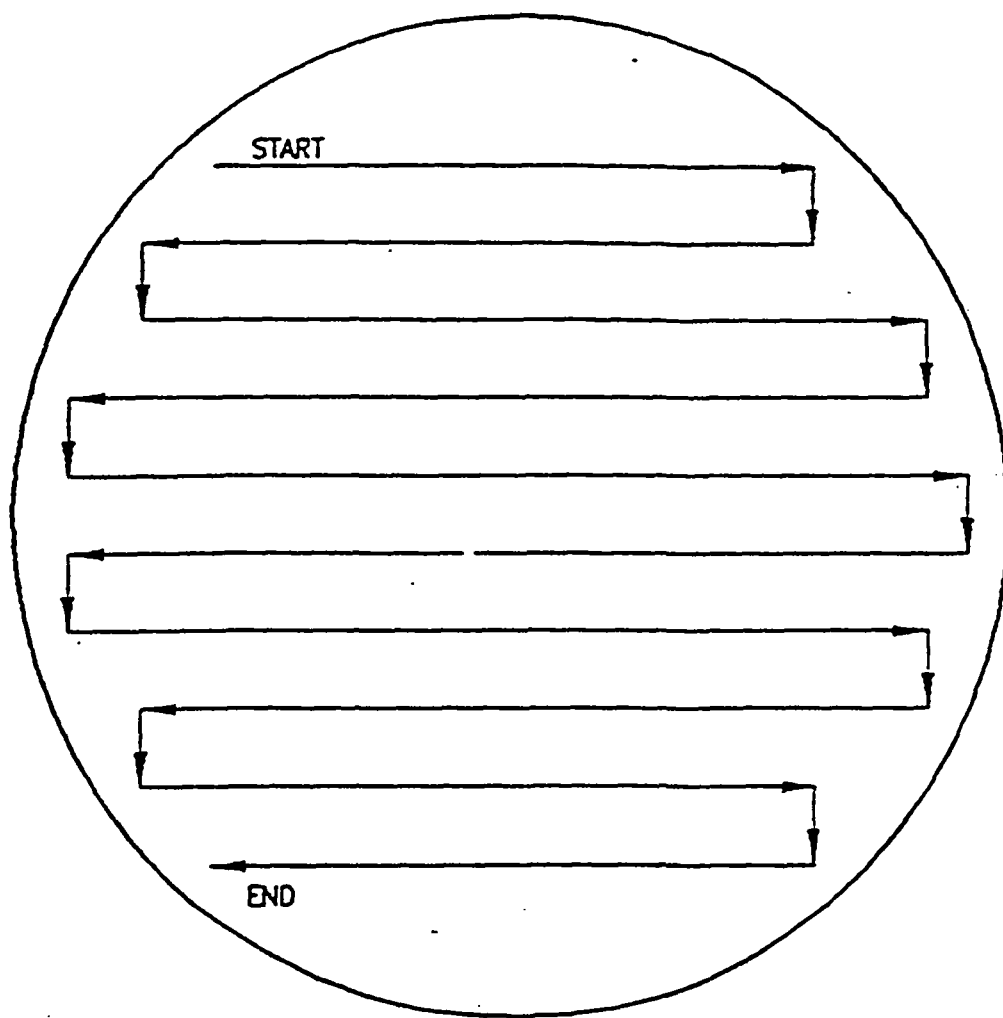
The portion of the sample examined in the second pass, under the higher magnification, will depend on the time available, the number of metal-bearing particles, and the complexity of metal mineralogy.

A maximum of 8 hours will be spent per sample.

8.3 DATA PRESENTATION

Analyst will record data as they are being acquired from each using the LEGS software, which places all data in a spreadsheet file format, Figure 8.2. Columns have been established for numbering the metal-bearing phase particles, their identity, size of longest dimension in microns, along with their association (L = liberated, R=rimming, I=included). The analyst may also summarize his/her measurements and observations in the formatted data summary files.

The frequency of occurrence and relative metal mass of each metal-bearing form as it is distributed in each sample will be depicted graphically as a frequency barograph. The particle size distribution of metal-bearing forms will be depicted in a histogram. Size histograms of each metal-bearing form can be constructed from data in the file.



FIRST PASS AT 40-100 X
SECOND PASS AT 300-600 X

DATA ACQUISITION SHEET

ASSAY (ppm):

SAMPLE I.D.: _____

LAB:

ANALYST: _____

TIME END:

TIME START: _____

DATA ACQUISITION SHEET

[illegible]

1. Sample #: L-79 B1 LST 01 911109			Pb Assay: 4 570		Type: SOIL	Lab: SSW		
2. Minerals		Chemical Formula	Freq.	T Area, μm^2	Area, %	Freq. = Length		
						Total, μm	L. %	med.
Jalena:	Ge	PbS						
Anglesite:	Ang	PbSO ₄	8			68.69	0.62	8.39
Cerussite:	Cer	PbCO ₃	123			5222.63	46.85	19.85
Pb oxide:	PbO	Pb ₂ O ₃						
PbO/carbonate:	PbO?							
Metallic Pb:	Pb	Pb						
Pb phosphates:	PbPhos		44			2554.16	22.91	33.71
Pb-Fe sulphate:	PbFeSul							
Pb arsenate:	PbArs							
Pb vanadate:	PbVan							
Wulfenite:	Wulf	PbMoO ₄						
Mn-Pb oxide:	MnPbO		31			2915.87	26.16	42.58
Fe-Pb oxide:	FePbO							
Pb-bearing barite:	PbBar							
Slag:	Slag		2			385.71	3.46	192.86
Pb silicate:	PbSi							
Pb-bearing C-matter	Pb(org)							
Paint:	Pnt							
Solder:	Sold							
Pb sulfosalt:	PbSfs							
Pb antimonate:	PbAnt							

3. Association:

Cerussite is liberated (100), enclosed (13) in silicate, FeO or silicate aggregates or intergrown with or cementing (10) quartz, silicate, Fe-sulphate or FeO. PbPhos is liberated (28), intergrown with or cementing (12) FeO, MnPbO or silicate or enclosed (4) in silicate aggregates. MnPbO is intergrown with or cementing (16) FeO, silicate or quartz, enclosed (12) in silicate aggregates or liberated (3). Anglesite is enclosed (6) in silicate or liberated (2). Slag is liberated.

4. Pb Mineralogical Distribution:

VALIDATED 6/4/93 (U.T.)

5. Species Bearing Ag x: As □; Bi □; Cd □; Hg □; Se □; Ti □ Observed

Signature of Analyst: Wendy Dren 10/4/93

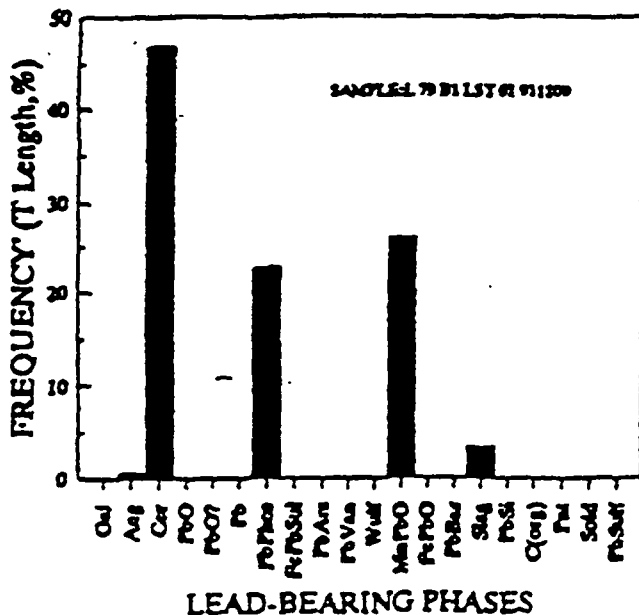


FIGURE 8.3

8.4 ANALYTICAL PROCEDURE

Prior to EMPA examination a brief optical examination of each sample will be made. This examination may help the operator by noting the occurrence of slag and/or organic matter.

Standard operating conditions for quantitative and qualitative analyses of metal-bearing forms are given in Table 8.1. Quality control will be maintained by analyzing standards at regular intervals and duplicates (see next section).

The backscattered electron images will be examined using two settings: one for light-element matrices (slag or organic) and the second for heavy-element matrices (lead sulfide or lead carbonate ect.).

Thus, no metal-bearing minerals will be missed during the scanning of the polished grain mount. The scanning will be done manually in a manor similar to Figure 8.1. Typically, the magnification used for scanning all samples except for airborne samples will be 40-100X and 300-600X. The last setting will allow the smallest identifiable (1-2 μm) phases to be found. Once a candidate particle is identified, then the backscatter image will be optimized to discriminate any different phases that may be making up the particle or defining its association. Identification of the metal-bearing phases will be done using both EDS and WDS on a EPMA, with spectrometers peaked at S, M(metal of concern), O, and C. The size of each metal-bearing phase will be determined by measuring in microns the longest dimension. A maximum of 8 hours will be spent in scanning and analyzing each mount.

Quantitative analyses:

Quantitative analyses are required to establish the average metal content of the metal-bearing minerals, which have variable metal contents such as: Fe-(M) sulfate, Fe-(M) oxide, Mn-(M) oxide, AsMO, PbMO, phosphate, and slag, Table A6.0. These determinations are important, especially in the cases of AsMO, PbMO, and slag which are expected to have considerable variation in their

dissolved metal content. Results will be analyzed statistically to establish mean values. These values are then used to determine relative mass of arsenic (RM_{As}) in each sample. They may also be depicted as histograms to show the range of metal concentrations measured as well as the presence of one or more populations in terms of metal content. In the latter case, non-parametric statistics may have to be used or the median value has to be established.

Associations:

The association of the metal-bearing forms will be established from the backscattered electron images. Particular attention will be paid in establishing whether the grains are totally enclosed, encapsulated or liberated. The rinds of metal-bearing grains will be identified. Representative photomicrographs of backscatter electron images establishing the association of the principal metal-bearing forms will be obtained for illustration purposes. A positive/negative, black and white film (Polaroid 55) will be used or a 128x128 (minimum) binary image in TIFF format may be stored. Recorded on each photomicrograph and negative will be a scale bar, magnification, sample identification and phase identification. Abbreviations for the identified phases should be used, examples are listed in Table 8.2. A final list must be submitted with laboratory report.

Table 8.1 EMPA Standard Operating Conditions.

	WDS	EDS
Accelerating Voltage	15 KV	15-20 KV
Beam Size	1-2 microns	1-2 microns
Cup Current	10-30 NanoAmps	10-30 NanoAmps
Ev/Channel	NA	10 or 20
Stage Tilt	NA	Fixed
Working Distance	NA	Fixed
MCA time Constant	NA	7.5-12 microseconds
X-ray lines**	S K-alpha PET O K-alpha LDE1 C K-alpha LDEC Zn K-alpha PET As L-alpha TAP Cu K-alpha LIF Cd L-alpha PET Pb M-alpha PET Pb L-alpha LIF	S K-alpha 2.31 KeV O K-alpha 0.52 KeV C K-alpha 0.28 KeV Pb M-alpha 2.34 KeV Pb L-alpha 10.5 KeV Mo K-alpha 17.5 KeV Zn K-alpha 8.63 KeV Cu K-alpha 8.04 KeV As K-alpha 10.5 KeV As L-alpha 1.28 KeV Cd L-alpha 3.13 KeV

** X-ray lines for other elements are selected for maximum intensity and minimum spectral overlap.

Table 8.2 Suggested Abbreviation for Photomicrographs.

Metal-bearing Phase	Abbreviation
Lead Sulfide	Ga
Lead Sulfate	Ang
Lead Carbonate	Cer
Mn-(M) Oxide	Mn(M)
Fe-(M) Oxide	Fe(M)
(M) Phosphate	(M)Phos
Fe-(M) Sulfate	Fe(M)Sul
Arsenic-Metal Oxide	AsMO
Lead Arsenate	PbAsO
Slag	Slag
Metallic Phase	(M)
Metal Silicate	(M)Si
Solder	Sold
Paint	Pnt
Metal-bearing Organic	(M)(Org)
(M) barite	(M)Bar
Arsenopyrite	Aspy

M = dominant metal found

8.5 INSTRUMENT CALIBRATION and STANDARDIZATION

At the beginning of each analytical session the WDS will have spectrometers "peaked" for M (metal of concern), C, O, and S on the appropriate crystals using mineral standards. The EDS will have MCA (multi-channel analyzer) calibrated for known peak energy centroids. Calibration will be made so as to have both a low (1.0-3.0 KeV) and a high (6.0-9.0 KeV) energy peaks fall within 0.05 KeV of its known centroid.

Once a week the magnification marker on the instrument will be checked following manufacturer instructions or by measurement of commercially available grids or leucite spheres. Size measurements must be within 4 microns of certified values.

Since most of the phase identification procedures used in this SOP are based on semi-quantitative methods, daily standardization for all elements is not essential. Visual verification of an element such as phosphorous or silica from an EDS spectra will be sufficient. However, due to the spectral overlaps encountered by (Pb-S-Mo) and (As-Mg-Pb) and the difficulty in detecting oxygen and carbon it will be important to check their standardization routinely.

At the beginning of each analytical session or once every 24 hours a set of mineral or glass standards will be run quantitatively for M (metal of concern), S, O, and C. If elemental quantities do not fall within +/- 5% of certified values the element must be recalibrated.

The metal-bearing forms in these samples will be identified using a combination of EDS, WDS and BEI. Once a particle is isolated with the backscatter detector, a 5 second EDS spectra is collected and peaks identified. The count rates for M (metal of concern), S, C, and O can be either visually be observed on the wavelength spectrometers or k-ratios calculated.

8.6 ARCHIVAL OF DATA

The laboratory is able to archive 100% of all EDS spectra and particle images; however, this is generally not done and only a representative population of metal-bearing particle images, and spectra are stored.

9.0 PERSONNEL HEALTH AND SAFETY

Each individual operating the KEVEX x-ray fluorescence or electron microprobe instruments will have read the "Radiation Safety Handbook" prepared by the University (Quick Reference Guide and Table of Contents are supplied in Appendix A.) and follow all State guidelines for operation of x-ray equipment.

During preparation of sample cups researchers will wear latex gloves and particulate mask. All material that comes in contact with the samples or used to clean work surface areas will be placed in poly-bags for disposal.

10.0 FINAL REPORT

A final laboratory report will be provided the CDPHE. The report will include all EMPA data including summary tables and figures. Individual sample data will be provided on disk.

Speciation results will include; 1) A series of tables summarizing frequency of occurrence for each metal phase identified along with a confidence limit, 2) Summary histograms of metal phases identified for each waste type, 3) A summary histogram of particle size distribution in each waste type, and 4) A summary of metal phase associations. Representative photomicrographs or TIFF images will also be included in the final report.

11.0 REFERENCES

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